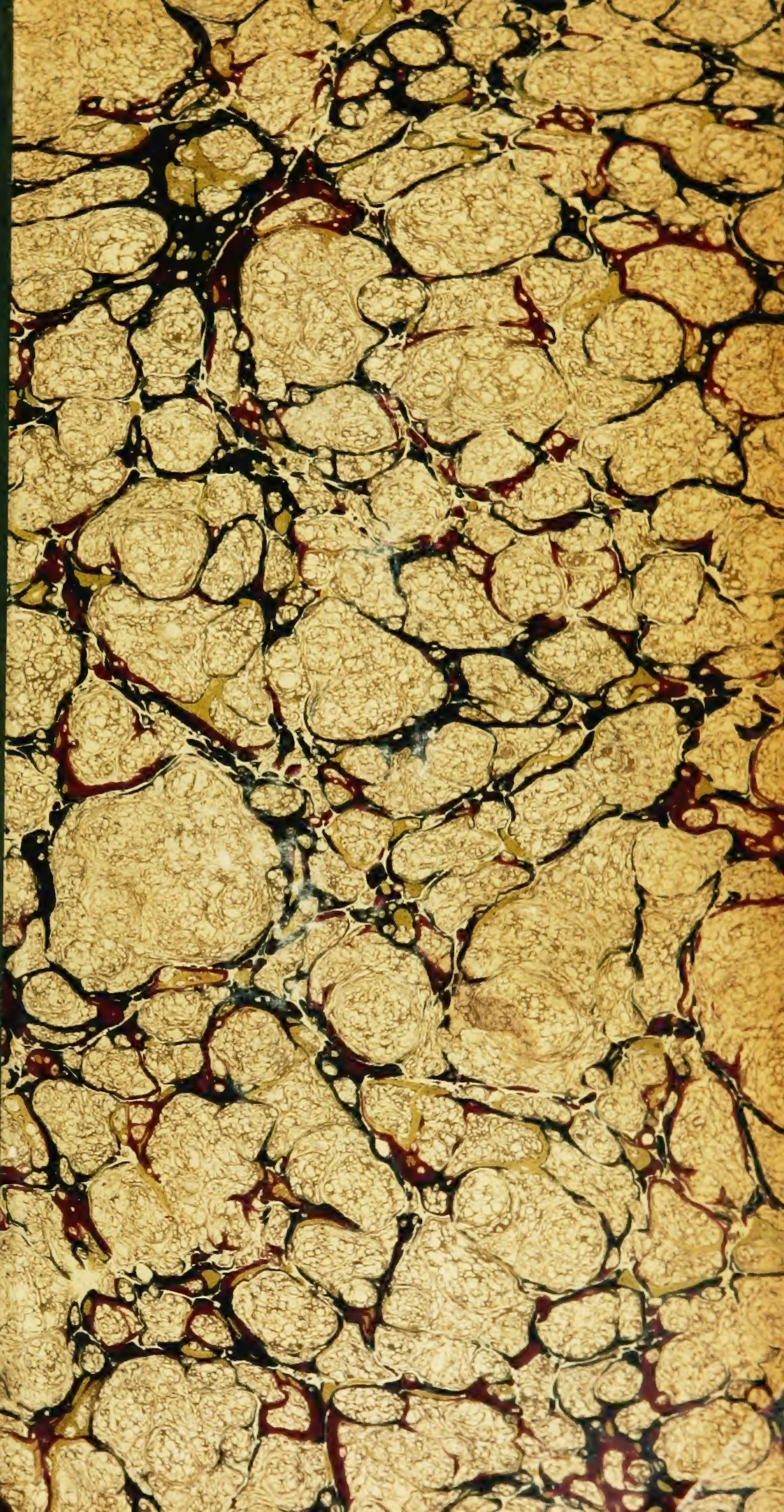

8583
P 8
XXV

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ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

APPENDIX

SECTION I TO SECTION Ve

VOL. XXV

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8583
P8
XXV

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TO THE

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VOLUME XXV

APPENDIX—SECTION I TO SECTION Ve

CONTENTS

Section I. Analytical Chemistry

Page

Breyer, Frank C.
A Quantitative Estimation of Small Amounts of Cadmium in the Dry Way 1

Breyer, Frank G.
A Proposed Standard Method of Analysis for Zinc 7

Castañares, Adolfo P.
A New Method for the Analytical and Quantitative Separation of Mercury from Bismuth 39

Lessing, R.
Report of the Sub-Committee on Standardisation of Methods on Determining Water in Coals and Other Fuels and in Minerals of the International Committee on Analyses 41

Merkel, E.
Vorschläge für Einheitliche Benutzung der Atomgewichtstabellen 91

Noyes, A. A.
Report of the Committee on Standard Methods for Determining Small Hydrogenion Concentrations 95

Spear, Ellwood B. and Strahan, Samuel S.
The Determination of Zinc by Electro-Analysis 97

Strahan, Samuel S. (see Spear, Ellwood B.)

Section II. Inorganic Chemistry

Baskerville, Charles and Riederer, H. S.
The Production of Chlorine Substitution Products of Methane from Natural Gas 105

Childs, D. H.
Action of Some Fluorine Compounds on Clay, Water, etc. 115

COWLES, ALFRED H. PAGE
Alumina, Hydrochloric Acid, Caustic Alkalis, and a White Hydraulic Cement by a New Process from Salt, Clay and Lime 119

COX, MARSHALL W. (see RICHARDS, THEODORE W.)

DUGGAN, THOMAS R.
Zeolites, Natural and Artificial 125

ENGLER, C.
Molekülverbindungen als Primärstufen Chemischer Reaktionen 131

NEUMANN, DR.
Report of the Verein Deutscher Chemiker with Regard to the International Regulation of Standards on the Literature of Mineral Acids to the Eighth International Congress of Applied Chemistry in New York 141

PALMAER, W.
On the Method of Producing Bicalcic Phosphate with the help of Electrolytically Produced Acid and Alkali 145

RICHARDS, THEODORE W. AND COX, MARSHALL W.
The Anhydrous Condition and Stability of Fused Lithium Perchlorate, and their Bearing upon the Atomic Weight of Silver 157

RIEDERER, H. S. (see BASKERVILLE, CHARLES).
RUFF, OTTO
Ueber die Zustandsdiagramme des Kohlenstoffs mit Eisen, Nickel, Cobalt und Mangan 163

URBAIN, G.
Sur la Nomenclature des Sels Complexes de la Chimie Minerale 177

Section IIIa. Metallurgy and Mining

ADAN, ROBERT
Micrographie des Fontes Speciales Pour Bagues de Pistons 185

BURRELL, GEORGE A. AND SEIBERT, FRANK M.
Errors in Gas Analyses Resulting from the Assumption that the Molecular Volumes of all Gases are Alike 189

GREENE, ALBERT E.
Electric Heating and theRemoval of Phosphorus from Iron 191

DOANIDES, J. P.
Sur les Creusets des Fours à Plomb 201

PAGE

SEIBERT, FRANK M. (see BURRELL, GEORGE A.)

THIESSEN, REINHARDT
On the Constitution and Genesis of Certain Lignites and Sub-Bituminous Coals 203

VON BAUR, C. H.
Electric Induction and Resistance Furnaces for Steel 205

Section IIIb. Explosives

COMEY, ARTHUR M. AND HOLMES, FLETCHER B.
The Use of the Ballistic Mortar for Determining the Strength of Explosives 209

COMEY, ARTHUR M. AND HOLMES, FLETCHER B.
Methods for the Determination of the Effective Strength of High Explosives 217

HOLMES, FLETCHER B. (SEE COMEY, ARTHUR M.)

KIBLER, A. L.
The Hydronitrides 235

KIBLER, A. L.
The Synthesis of Mercury Fulminate from Propyl Alcohol 239

MUNROE, CHARLES E.
Development in Explosives in the United States During the last Three Years 245

REPORTS OF COMMISSIONS
Commission Internationale pour L'Etude de L'Unification des Méthodes D'Épreuves sur la Stabilité des Explosifs 255
International Commission for Unification of the Testing Methods on the Stability of the Explosives 305

Section IIIc. Silicate Industries

ADAN, ROBERT
Rapport sur les Propriétés des Ciments Portland Artificiels Belges . . . 315

LANDRUM, ROBERT D.
The Function of the Various Raw Materials in a Sheet Steel Enamel . . 317

Section IV. Organic Chemistry

BASKERVILLE, CHARLES
Ethyl ether by Catalysis 327

PAGE

BENSON, H. K.
Chemical Treatment of Waste Wood 331

BIILMANN, EINAR AND MADSEN, ERIK HOST
The Action of Potassium Xanthogenate on Halogen-Malonic Acids .. 339

BROWN, HAROLD H. (see FRANKFORTER, GEORGE B.)

CLAFLIN, ALAN A.
The Products of the Lactic Fermentation of Sugars 343

CLAFLIN, ALAN
The Present Status of the American Tanning Industry 347

CONE, L. H.
The Salts of Acridine, Pyridine and Quinoline 349

CROSSLEY, M. L.
An Improved Method for the Production of Mono-B-Amido Anthraquinone 351

CURTISS, RICHARD SYDNEY AND HEWES, CHARLES K.
Intermediate Addition Products in the Reactions of Organic Chemistry: The Mechanism of the Reaction in the Formation of Hydrazones... 353

CURTISS, RICHARD SYDNEY AND SHEWADE, VANAYAK YESHAWANT
The Mechanism of Hydrazon Formation with Ethyl Oxomalonate ... 355

DANIELS, E. A. (see HUNTER W. H.)

DUPONT, JUSTIN AND LABAUNE, LOUIS
Extrait 357

EDWARDS, J. D. (SEE HUNTER, W. H.)

FRANKFORTER, GEORGE B. AND BROWN, HAROLD H.
The Chemistry of Wood—The Resins of the Douglas Fir 359

FRANKFORTER, GEORGE B. AND KRITCHEVSKY, W.
Contributions to our Knowledge of the Condensation Reaction by Means of Aluminum Chloride 361

FRANKFORTER, G. B. AND POPPE, F. W.
Contributions to our Knowledge of the Terpenes. Polymerization of Pinene 363

GOMBERG, M.
Ethers or Oxides in the Triphenylmethane Series 371

HANRIOT, M.
Sur la Recherche de L'Ionone 373

HEWES, CHARLES K. (SEE CURTISS, RICHARD SYDNEY)

Hudson, C. S. Page
The Kinetics of the Inversion of Sucrose by Invertase 375

Hunter, W. H. and Edwards, J. D.
An Improved Apparatus for the Determination of Carboxyl Groups in Organic Acids 377

Hunter, W. H., Daniels, E. A., Olson, A. O., and Karatz, L.
A Catalytic Decomposition of Some Phenol Silver Salts by Alkyl Iodides 393

Karatz L. (see Hunter, W. H.)

Kloud, Jan (see Krauz, Cyrill)

Komppa, Gust
Über die Totalsynthese des Fenchocamphorous 395

Krauz, Cyrill and Kloud, Jan
Sur les Cyanhydrines de Quelques Monosaccharides 397

Kritchevsky, W. (see Frankforter, George B.)

Labaune, Louis (see Dupont, Justin)

Leech, Paul (see Stieglitz, Julius)

Madsen, Erik Host (see Biilmann, Einar)

Marcusson, J.
Die Zusammensetzung der Hochsiedenden Mineralöle 403

Olson, A. O. (see Hunter, W. H.)

Poppe, F. W. (see Frankforter, George B.)

Potměsel, R. (see Votocek, Emil)

Raikaw, P. N.
Neue Methode zur Identifizirung des Methylalkohols 417

Rassow, B.
Ueber Rizinusolsäure 421

Reddick, Guy (see Stieglitz, Julius)

Reid, E. Emmet
Studies in Esterification V[1]*: The Esterification of Amides and Thio-Amides and the Formation of Dithio Esters* 423

Ruttan, R. F.
Margaric Acid and Its Relations to Palmitic and Steric Acids 431

PAGE

SHEWADE, VANAYAK YESHAWA (SEE CURTISS, RICHARD SYDNEY)

STIEGLITZ, JULIUS, REDDICK, GUY, AND LEECH, PAUL
The Molecular Rearrangement of Triphenylmethylhydroxylamin 443

STIEGLITZ, JULIUS AND VOSBURGH, ISABELLE
The Molecular Rearrangement of Triphenylmethylbromamin 445

VESELY, V.
Sur Quelques Dérivés du Diphénylfurylméthane 447

VESELY, V.
Contributions à L'Etude des Rosamines 449

VOSBURGH, ISABELLE (SEE STIEGLITZ, JULIUS)

VOTOCEK, EMIL AND POTMESEL, R.
Sur le Dosage de la Phloroglucine 453

YABUTA, TEIJIRO
On Koji Acid, a New Organic Acid Formed by Aspergillus Oryzae... 455

Section IVa. Coal Tar Colors and Dyestuffs

DOYLE, AIDA M. (see WILEY, HARVEY W.)

GREEN, ARTHUR G.
Quinonoid Addition as the Mechanism of Dyestuff Formation 463

SMITH, E. E.
Coal-Tar Colors and Injury to Health 473

WARD, L. DACOSTA
The Need of Official Tests in Dyeing and Textile Chemistry 475

WILEY, HARVEY W. AND DOYLE, AIDA M.
Use and Detection of Coloring Matters in Foods 477

Section Va. Industry and Chemistry of Sugar

AULARD, A.
Fabrication D'Une Farine Sucrée de Betterave "Beetmeal" son Emploi dans L'Alimentation Humaine et Animale 479

AULARD, A.
La Dessiccation des Produits Végétaux et des Sous Produits Industriels S'Impose-t-Elle? 485

PAGE

AULARD, A.
L'Emploi de la Cellulose (Pâte à Papier) Comme Produit Filtrant dans L'Industrie Sucrière et Autres 489

AULARD, A.
Quelle que soit la Température (90 à 150° Centigrades) à Laquelle on Soumet les Solutions de Saccharose de Glucose, de Maltose, etc., Pures ou Impures, ces Hydrates de Carbones Peuvent ils se Transformer en Caramel, ou l'un de ses Dérivés, en Milieu Humide a L'Abri de L'Air? . 493

AULARD, A.
Quelques Particularitiés Nouvelles sur L'Emploi de L'Anhydride Sulfureux et des Hydrosulfites dans L'Industrie Sucrière 501

AULARD, A.
Sur la Cristallisation de la Saccharose en Milieu Plus au Moins Impur 505

ANDRLÌK, K. ET STANEK, V.
Etude Chimique sur la Carbonatation 509

ANDRLÍK, K. ET URBAN, J.
Sur les Relations Entre la Richesse Saccharine des Racines et les Caractères Chimiques des Descendants D'Une Betterave-Mere dans le Première Génération 511

ANDRLÍK, K. ET URBAN, J.
Variabilité de la Consommation de L'Azote des Descendants D'Une Betterave Porte-Graine dans la Première Génération 513

ANDRLÍK, K. ET URBAN, J.
Variabilité de la Composition Chimique des Descendants D'Une Betterave Porte-Graine dans la Première Génération 515

BATES, FREDERICK J. AND JACKSON, RICHARD F.
A Revision of the Hundred Point of the Saccharimeter 517

BROWNE, C. A.
A Constant Temperature Laboratory for the Polarization of Sugars . . 519

CROSS, WILLIAM E.
Sour Cane in Louisiana 531

JACKSON, RICHARD F. (see BATES, FREDERICK J.)

ROBERTS, CHARLES C.
Determination of Sucrose in Confectionery Containing Cooked Starch and in Marshmallows 539

SALLARD, E.
Le Sucre Clerget des Mélasses Normales de Betteraves par Double PolarisationNeutre 541

PAGE

STANEK, V. (see ANDRLÍK, K.)

URBAN, J. (see ANDRLÍK, K.)

Section Vb. India Rubber and other Plastics

BAEKELAND, L. H.
Phenol-Formaldehyde Condensation Products 563

BEADLE, CLAYTON AND STEVENS, HENRY P.
The Nature of the Resinous Constituent and Its Influence on the Quality of Rubber 581

CRANE, JASPER E.
The Prolonged Action of Mixed Acid on Cellulose 587

FOX, CHARLES P.
So-Called "Osage Orange Rubber"—A Product of Kansas 593

STEVENS, HENRY P. (see BEADLE, CLAYTON)

WHITBY, G. STAFFORD
On some Preliminary Observations Regarding the Causes of Natural Change in the Latex of Hevea Brasiliensis; and on the Depolymerisation of Caoutchouc and its Conversion 597

Section Vc. Fuels and Asphalt

ADAMS, GEORGE O. (see CLARK, H. W.)

AYRES, W. S.
The Technical Problems of Coal Preparation 623

BARNES, GEORGE W.
The Use of Natural Gas in Steam Boilers 625

BASKERVILLE, CHARLES AND HAMOR, W. A.
American Oil Shales 631

BUCH, N. W. (see ULLMANN, H. M.)

BURRELL, GEORGE A. AND SEIBERT, FRANK M.
The Extraction of Gasoline from Natural Gas 635

BURRELL, GEORGE A. AND SEIBERT, FRANK M.
Composition of Some Natural Gases 637

CLARK, H. W. AND ADAMS, GEORGE O.
Methods and Reasons for Analyses of Bituminous Material by the Massachusestts Highway Commission 639

PAGE

DECLUY, M. HENRY
Les Emplois Industriels du Coke de Gaz en France 645

DUNSTAN, ALBERT ERNEST AND STREVENS, J. F.
Technical Applications of Viscosity 647

ENGLER, C.
Ein Beitrag zu der Frage der Bildung des Asphalts 661

FOSTER, WILLIAM
A Remarkable Carbonaceous Clay Deposit near Putnam, New Mexico 667

GRINE, HARRY A.
Crude Oil Gas Producers of the Pacific Coast 669

HAMOR, W. A. (see **BASKERVILLE, CHARLES**)

HARDING, E. P. AND JOHNSON, EINER
An Apparatus and Method for Determining Hydrogen Sulphide in Illuminating Gas 673

HOLDE, PROF. DR.
Die Zähigkeitsbestimmung von Fluessigen Schmiermitteln 677

HUBBARD, PRÉVOST AND REEVE, C. S.
The Effect of Exposure on Bitumens 683

JOHNSON, EINER (see **HARDING, E. P.**)

JOHNSON, NORWOOD
The Use of Natural Gas in the Manufacture of Open Hearth Steel 685

LEWIS, RICHARD H. (see **REEVE, CHARLES S.**)

MALCOLMSON, CHARLES T.
Commercial Aspects of the Coal Briquetting Industry 687

MCDOWELL, J. C.
Industrial Conditions of the Utilization of Natural Gas 701

PHILLIPS, FRANCIS C.
The Determination of Soot Produced by Mine Lamp Oils 711

PHILLIPS, FRANCIS C.
The Composition of Natural Gas 719

RAKUSIN, M. A.
Ueber die Beziehungen Zwischen der Chemie der Erdöle und der Geologie Derselben 721

PAGE

REEVE, CHARLES S. AND LEWIS, RICHARD H.
Application of the Dimethyl Sulphate Test for Determining Small Amounts of Petroleum or Asphalt Products in Tar 727

REEVE, C. S. (see HUBBARD, PRÉVOST)

SADTLER, S. P.
Petroleum Analytical Methods 729

SEIBERT, FRANK M. (see BURRELL, GEORGE A.)

STEINSCHNEIDER, LEO
Neuerungen auf dem Gebiete der Destillation Hochsiedender Oele.... 735

STREVENS, J. F. (see DUNSTAN, ALBERT ERNEST)

TIMMERSBACH, OSCAR
Ueber die Verwendung von Nicht Vorgewaermten Koksofengas im Martinofen 745

UHLIG, E. C.
The Analysis of Water Gas Purification Material 765

UHLIG, E. C.
The Determination of Tarry Matter in Water Gas Purification Material 769

ULLMANN, H. M. AND BUCH, N. W.
The Rapid Determination of Ash in Coal 771

WHITE, DAVID
Resins in Paleozoic Coals 775

Section Vd. Fats, Fatty Oils and Soaps

MARCUSSON, J.
Die Bestimmung des Seifengehalts Konsistenter Fette 777

Section Ve. Paints, Drying Oils and Varnishes

PIERRES, GASTON DE
The Struggle Between White Pigments in Europe 783

POTSDAMER, LOUIS SAMTER
A Method for the Detection of Adulteration of China Wood Oils 791

THOMPSON, GUSTAVE W.
The Coating Power and the Hiding Power of Paints 795

A QUANTITATIVE ESTIMATION OF SMALL AMOUNTS OF CADMIUM IN THE DRY WAY

Frank C. Breyer
Palmerton, Pa.

A quick method of estimating whether an ore or zinc product contains less than 0.05% cadmium, or none at all, would in many cases save the necessity of the painstaking separating of cadmium, either by hydrogen sulphide or electrolytically, in zinc analysis.

In a gravimetric or electrolytic zinc determination, the error caused by not separating 0.05% cadmium would be but very little greater than that involved in the separation of the cadmium beforehand. When the zinc is determined by titrating with ferrocyanide, the error caused by the presence of 0.05% cadmium is about 0.03% or just about equal to that involved in a previous separation of this small percentage of cadmium.

An article by R. Biewend, Berg-und Huettenmaennische Zeitung 32 (1902) pages 400–413–425, gives several quick and wonderfully sensitive dry tests for cadmium. They are all apparently too sensitive to be used for the above purpose, so a modification was tried of his original closed tube method, which latter consists in heating carefully, the previously roasted material to be tested, with a variety of reducing agents such as ferrous carbonate, iron, manganese, aluminum and magnesium. The mirror of metallic cadmium resulting can then be recognized by either dropping a little sulphur into the tube and running it with the flame out over the mirror, giving the brilliant cadmium sulphide, red when hot, and yellow when cold, or by cracking the lower end of the tube thus admitting air, and volatilizing a ring of the brown oxide. This method gave, on trial, excellent tests when only a hundredth of a percent of cadmium was present. Biewend showed that, under these conditions, no other metal gave a mirror that could be taken for cadmium.

A Rose crucible was substituted for the closed tube, and through the Rose stem a very small stream of air, saturated with gasolene vapor (ordinary gasolene laboratory gas), was allowed to pass. The crucible was heated to bright redness with the blast lamp.

At first, the sample, previously roasted to remove water, higher arsenides, selenium, sulphur and other sublimate yielding gases and materials, was mixed with an equal bulk of iron or aluminum powder before heating in the Rose crucible, but just as satisfactory results were obtained without pre-roasting or the addition of the iron or aluminum.

With the lid on the crucible, the method also gave a satisfactory test for arsenic when as little as 0.05% was present. The arsenic always settled in a black patch on the lid around the hole for the stem, as well as in a ring around the stem itself just outside the lid.

When cadmium alone was being tested for, the lid of the crucible was left off, the stem merely projecting into the crucible and being held in place by a clamp.

The method consists in the following procedure: 200 mgs. of the material to be tested are weighed out roughly; placed in the bottom of a Rose crucible; the Rose stem is introduced, nearly touching the material on the bottom, and a very small stream of gas allowed to pass through, enough to give, when lit, a flame ¼ inch long.

The crucible is then gradually heated to bright redness and kept there until streams of zinc oxide are seen rising. The flame is then removed, and, when the crucible is cool, a ring or patch of brown red cadmium oxide will appear on the side of the crucible at the level where it is supported on the outside by a piece of heavy asbestos board with a hole in it. The board also serves to keep the top of the crucible cool enough to condense the cadmium before it escapes from the crucible.

If there is present in the sample as little as 0.1% cadium, the oxide is still plainly visible. With increasing proportions of cadmium, the patch becomes a perfect ring of increasing breadth and density, covering the Rose stem as well. A little experience will enable one to estimate, from the relative density of this sublimate, to within 0.1% of the amount of cadmium present.

The author tried this, with excellent results, on numerous ores containing up to 0.6% cadmium.

If 200 mgs. of the sample give no brown coating, there is less than 0.1% cadmium present. If 400 mgs. give a slight coating, there is between 0.05% and 0.1%. This was the accuracy desired to save the electrolytic or sulphide separation of cadmium in zinc analysis.

The possibility of mistaking other coatings for cadmium was eliminated by adding successively Sb_2O_3, PbO, PbS and Bi_2O_3 to a Willemite ore, which was subsequently shown to hold only a few thousandths of a percent of cadmium, and which gave no test by this method. Neither bismuth nor lead gave any coating, while antimony gave a black ring, less volatile than arsenic, but still settling above cadmium and always dense black, never red-brown or yellowish-brown.

It seemed worth while to try the closed tube method, as given by Biewend for the detection of very small quantities of cadmium, on the Franklin Furnace ores, oxide and spelter.

The method, in full, consists in heating the pre-roasted sample with some reducing agent, as mentioned above, or, in the case of metallic zinc or zinc alloys, alone in a closed tube of about 5 mm. internal diameter and about 5 cm. long. In case the sample contains ferrous iron or bitumen, it is unnecessary to add a reducing agent.

If the sample contains cadmium, a sublimate of the metal, oxide, or sulphide, depending on the conditions, will appear a little way above the material. To distinguish the metallic ring from zinc, which is likewise volatilized in a ring just beneath the cadmium, a little sulphur may be added or air admitted, by cracking the lower end of the tube, giving in either case, characteristically colored compounds.

For very small traces of cadmium, 0.001% in ores and light compounds and 0.0005% to 0.0001% in spelter and alloys, the tube is drawn out to capillary dimensions, just above the sample, after the latter has been added.

Using 200 mgs. of Willemite, without the addition of any reducing agent, since it contains ferrous iron and bitumen, no visible sublimate of cadmium was obtained when the tube was not drawn out. When the tube was drawn out to the diameter of a pin-head, a very plain metallic ring was obtained which, on dropping in a little flowers of sulphur and heating the tube sharply, gave the characteristic, cadmium sulphide, red when hot, yellow when cold. Crude ore and Franklinite gave identical results. In the case of Palmerton oxide, the cadmium was still plainly visible when the tube was only narrowed to about ¼ its original diameter.

With a spelter containing 0.1% cadmium, 2 mgs. gave, in the capillary, a very perceptible cadmium ring. Four hundred mgs. of Horse Head spelter failed to give, after five trials, the least trace of cadmium. All three draws were tested. This indicates that there is less than 0.0005% of cadmium in that spelter.

Prime spelter Western gave the test, even in the unnarrowed tube, in all three draws.

These two methods have another value, aside from saving the separation for cadmium in zinc analysis when that metal is not present or only there in small quantities, namely, saving the long wet test for cadmium in cadmium analysis, when the sample contains less than a couple hundredths percent of cadmium or none at all. The only safe wet test requires a long evaporation to appearance of sulphuric fumes and two or possibly three separations with hydrogen sulphide before one can say for certain whether cadmium is present or not.

To show the value of the methods, the following samples were estimated and then run by the regular laboratory methods, which is accurate to within 0.03% to 0.05%.

	Cadmium Estimated—Dry Way	Cadmium Regular Analysis
Zinc Sludge	0.5%	0.59%
A Limestone	0.001%-0.005%	None
B Tailings	0.001%-0.005%	”
C Black Iron	0.03%	Trace
D Oxide	0.03%	0.04%
6 Colorado Leadville Ores	0.07%	0.06%-0.12%

SUMMARY

The closed tube method of R. Biewend and a modification, in which a Rose crucible is substituted for the closed tube, give a very quick and apparently reliable method of estimating the amount of cadmium present in ores, oxides, alloys, spelter and the like, in quantities from 0.0005% to 0.6%.

The value of the methods depends upon the saving of unnecessary separations for cadmium in zinc analysis and long determinations for cadmium in cadmium analysis, when none or only traces of the metal are present.

A PROPOSED STANDARD METHOD OF ANALYSIS FOR ZINC

Frank G. Breyer
Palmerton, Pa.

An explanation for the appearance of this paper, proposing a standard method of analysis for zinc, before the International Congress of Applied Chemistry, seems necessary, since the excellent and very complete review and critical survey of the literature of zinc analysis presented by Dr. Nissenson before the VI International Congress at Rome, recommends any one of four methods as equally accurate and satisfactory for the analysis of ores and other zinciferous materials for zinc. The results of Nissenson's analyses, by the four methods, on a number of ores and products, show that with a proper understanding of any one of the methods, accurate results can be obtained on most ores and materials.

There are, however, certain important ores and zinc products for which all four methods are decidedly not equally satisfactory, as the report of the Zinc Committee of the American Chemical Society and the records of the New Jersey Zinc Company clearly show, when samples of the crude ore from Franklin Furnace, N. J., or of the magnetic separator product, Franklinite from this same ore, were sent out for analysis to various chemists. Other ores of high iron, manganese, cadmium or copper content cannot be worked satisfactorily by all four methods, and it therefore seems desirable to point out a standard method, which not only gives statisfactory results for ores and zinc materials of a high degree of impurity, but which has also been selected as the most satisfactory standard method for the common sulphide and carbonate ores, after a year's work devoted to determining the relative merits of the various methods of zinc analysis.

In 1903, the Committee on Uniformity in Technical Analysis of the American Chemical Society reported variations from 12.20

zinc to 39.22% zinc, on an ore of the character mentioned above, by chemists supposed to be familiar with zinc analysis. The result of the committee's work for the improvement of zinc analysis in America was the recommendation of the Modified Waring Method as a standard American method of analysis for zinc. The improvement, as shown by the report in 1907 of the Sub-Committee on Zinc Ore Analysis, due to the use of this method, was quite remarkable. The method, however, has not come into general use as a standard procedure, and most chemists who have expressed themselves in the journals, find it unsatisfactory.

The defects of the Modified Waring Method will be spoken of later in this paper. Another excellent reason for again discussing zinc analysis, is the fact that, practically none of the common American text-books or recent articles dealing with zinc analysis, show any signs whatever of their authors being aware of Dr. Nissenson's report.

HOW THE STANDARD METHOD WAS SELECTED

The work of collecting, classifying and digesting the literature of zinc analysis having been most clearly and carefully performed by Dr. Nissenson, the author merely tried to verify experimentally Nissenson's conclusion, namely; that there was little, if any preference between the four best known and most used methods: the gravimetric hydrogen sulphide method, the electrolytic method, the sodium sulphide method of Schaffner and the ferrocyanide method of Galletti. Since no one of these four complete methods is entirely distinct from the others, but each has some of the features common to one or more of the other three, a different basis of classification was adopted. Since we must be able to tell how much zinc is in a pure solution first, before we can say how much is in an impure one, the first and most logical step was to determine the relative merits of the various methods for determining zinc in pure solution, then the merits of the various methods of separating interfering elements, and lastly the merits of the various methods of solution of the zinciferous material.

The complete standard method then should be the best combination of the three fundamental operations.

BASIS OF SELECTION

In selecting the best method for each of the three fundamental operations, accuracy was the first point considered. Then the methods were judged as to the relative difficulty of maintaining, in every day work, the conditions required for the highest degree of accuracy. Lastly the influence of the time element was considered.

Wherever previous evidence is conclusive on a certain point, the author has omitted giving in detail his own data. The prime object to this paper is to give a clear understanding of the proposed standard method, therefore, wherever possible, details already covered by others or readily accessible in the literature, are omitted in the hope of presenting the method in toto with something like its proper balance.

THE DETERMINATION OF ZINC IN PURE SOLUTION

Gravimetric Methods

Weighing as Oxide

Numerous inorganic and organic precipitants for zinc have been proposed with subsequent ignition to oxide. Various objections have been raised against most of them, leaving but two of the simpler, that are used to any extent. The first of these, the precipitation as the carbonate, is in fairly common use today. Despite the fact that Classen [1] and Weiss [2] have both shown that the precipitate contains considerable amounts of silica and alkaline salts when the precipitation is made in glass-ware (platinum is seldom used). The necessity of using platinum eliminated this method for general use from further discussion, at least until the other methods showed equal disadvantages.

The conversion of the sulphide to oxide according to Weiss seemed to have many advantages, and was tried out as follows: Known weights of zinc, containing 0.026% of lead, 0.015% of iron and a few hundredths of oxide, were dissolved in hydrochloric acid and evaporated to the appearance of fumes with one or two c.c. of sulphuric acid. This solution was cooled, diluted, neutralized with the purest KOH, an excess of 100–200 mgs. of H_2SO_4 added, diluted to 100–150 c.c., and a rapid stream of hydrogen sulphide passed through at room temperature for forty minutes. The precipitate was allowed to settle a few minutes, and was then filtered off on a gooch. The precipitate was dried on the door of an electric muffle and then heated (800°–900° C.) in the muffle, to which the air had excess, for ½–1 hour to constant weight. Results accurate to within one milligram were obtained by this method, using up to five hundred milligrams of zinc in the tests.

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[1] Classen, Ausgewählte Methoden d. anal. Chem., 1901, 1 Bd., S. 330.

[2] G. Weiss Inaug.-Dissert. München 1906.

Weighing as Sulphide

Rose's Method

After a few trials, this method was abandoned as being less accurate, even when taking every precaution, more involved, and more time consuming than the simple weighing as oxide. Nissenson, however recommends this as more desirable than the weighing as oxide.

Weighing as Sulphate

Results as accurate as those obtained with the oxide method were obtained by simply evaporating carefully with excess of sulphuric acid over an asbestos gauze until fuming ceased. The advantage of the oxide method over the sulphate method lies chiefly in the fact that when zinc is separated from the rest of the elements it is precipitated as sulphide. The oxide can be obtained directly from this with practically no further attention, whereas the sulphate requires the resolution of the sulphide and the careful fuming process.

Phosphate Method

The phosphate precipitation of Tamm, Stone, Dakin, and also Waring and Stone, is less desirable than any of the common gravimetric methods, since the zinc after being separated as sulphide from the other elements, must be redissolved, the hydrogen sulphide boiled out, and the zinc then reprecipitated, after carefully neutralizing the solution, filtered, washed, dried and ignited. With all these additional operations the author was unable to obtain an accuracy of more than 3 mgs. in tests using up to five hundred mgs. of Zn. One of the main difficulties was the difficulty of washing the ammonium-zinc phosphate without loss. Only with the greatest precautions and attention can the phosphate method yield good results, as can readily be seen from Dakin's [1] paper.

Other Gravimetric Methods

None of the other gravimetric methods proposed have ever been used by more than the few who were concerned in originating them, as various reviewers of zinc literature remark.

VOLUMETRIC METHODS

Sodium Sulphide Method

The titration of zinc with a standardized sodium sulphide solution was not tried by the author for two reasons. First: because of the change in value of the sulphide solution, necessitating very frequent standardizations. Second: because various other authorities (DeKoninck & Prosst,[2] Nissenson,[3] and Voigt[4]), all state that as satisfactory or better results can be obtained by the ferrocyanide method, which has the advantage of needing restandardization very seldom when the solution is properly prepared in the first place. Another reason why the author never tried the sulphide method was, because, in experimenting with the ferrocyanide titration, a simpler and more accurate end point was found for the latter determination, and if the latter method was to be preferred, using the old end point, with the new end point the preference was still more decided.

[1] Dakin. Zeitschft. f. Anal. Chem., *39* (1900), 273.

[2] De Koninck & Prosst. Zeitschr. f. angew. Chem., *9* (1896), 460, 564.

[3] Nissenson, Loc. cit.

[4] Voigt, Zeitschft. f. Ang. Chem., 1911 p. 2195, 1912 pp. 205, 1005.

Potassium Ferrocyanide Method

Low's modification of the ferrocyanide titration was tried, since it seemed to possess all the good features of the ideal method as recommended by DeKoninck & Prosst[1] in their thorough and basic work on this titration, and in addition avoided the inconvenience and error due to two standards and a back titration, as recommended by the latter authorities. For a proper understanding of the ferrocyanide method, De Koninck & Prosst's article must be read in full.

A description, only of the modification used by the author, will be given here. The pure zinc solutions are made ammoniacal with 13 c.c. of ammonia (0.90 Sp. gravity), acidified and an excess of 3 c.c. of hydrochloric acid (Sp. gravity 1.2) is added. The metallic zinc or zinc sulphide should be dissolved in 10 or 12 c.c. of hydrochloric acid, so that 13 c.c. of the strong ammonia will always make the solution alkaline. Then, on neutralizing with hydrochloric acid, one is assured of always having the same amount of ammonium chloride present. This acidified solution is diluted to 200 c.c., heated to incipient boiling, and, after pouring out about a third into a small beaker, the remaining two-thirds are titrated and an excess of about 25% of the titrating solution added. The end point is determined in the usual manner with 1% uranium nitrate. All except a few c.c. of the reserve portion are then added, the end point again passed, this time by only a half of a c.c. of ferrocyanide, and then the last of the reserve portion added and the little beaker rinsed out with the whole portion. The end point is then carefully approached drop by drop. The advantages of this method of titration are that it prevents overrunning the end point, and, consequently saves the very cautious manipulation when titrating in one operation, and also insures the complete uniformity of the precipitate, owing to the excess of ferrocyanide, present twice, when the solution is titrated to an excess of the latter reagent.

Working by this method, the author titrated a zinc solution from a dissolved zinc sulphide precipitate, containing three or four tenths of a milligram of ferrous iron which had been retained with the zinc sulphide when the latter was precipitated from a solution containing almost equal quantities of iron and zinc. This solution containing the ferrous iron, when titrated, gave a strong turquoise-blue color, so long as the zinc was in excess, but a few drops before the end point, as obtained with uranium nitrate, it changed sharply to a pea green and with several more drops then quickly faded to a creamy yellow. On adding the greater part of the reserve portion of the zinc solution, the blue color appeared again just as strong as ever, again vanished when an excess of ferrocyanide was added, again appeared when the last portion of zinc was added and finally vanished a few drops before the final end point, as determined with uranium nitrate.

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[1] De Koninck and Prosst; Loc. cit.

This blue color has been mentioned by numerous writers on zinc determination and by some rightly ascribed to the presence of iron. No one, however, seems to have ever gotten more than a "trace of blue" or a "tinge of blue color." This may be due to another factor, mentioned below, as well as to the presence of but a trace of ferrous iron (0.1 mg. or less), whereas the first solution in which the author noticed the color particularly, contained, as previously stated, 3–4 tenths of a milligram of ferrous iron in the presence of 180 mgs. of zinc.

The value of this vanishing blue color as a warning of the approach of the uranium nitrate end point has been also commented upon, but the authors are always uncertain as to whether the blue color will appear at all. By experiment, the author found that freshly dissolved potassium ferrocyanide gave very little blue color with 3–4 tenths of a milligram of ferrous iron in the zinc solution, whereas a ferrocyanide solution that had stood for several months showed the blue color strongly. It was also found that the depth of the blue color increased with increasing amounts of ferrous iron. Since the only difference between the freshly prepared ferrocyanide and that which had stood for several months, is in the amount of ferricyanide present due to oxidation by the dissolved oxygen and carbon dioxide in the water, enough ferricyanide was added to the freshly prepared ferrocyanide to give the latter solution the same yellow tint as that possessed by the month's old ferrocyanide solution. On titrating with this solution, the blue color was just as strong and gave as sharp a change as the old solution.

The following explanation then offered itself. So long as zinc is in excess, all the ferrocyanide is removed as insoluble zinc potassium ferrocyanide; the ferricyanide, however, does not apparently act with the zinc, but gives the blue solution with the ferrous iron. When the zinc is all precipitated, the ferrocyanide decomposes the ferro-ferricyanide blue and gives the white or colorless ferro-ferrocyanide solution. The fact that it takes several drops to make the blue vanish completely to a creamy yellow, may readily be explained by mass action. The first drop of excess ferrocyanide, however, causes sufficient change in color, namely, from blue to pea green, to serve admirably as an indicator.

The author used the blue end point in connection with the regular uranium end point for some time, but soon found that he could determine the end point by the the change in the blue color about twice as sharply as he could with the uranium solution. Several hundred determinations using both end points jointly showed that the blue end point appeared just .25 of a c.c. before the end point with 1% uranium nitrate using a ferrocyanide solution one c.c. of which equals 5 mgs. of zinc. As for obtaining a ferrocyanide solution with the proper amount of ferricyanide, one can dissolve 44 grams, for a solution 1 c.c. of which equals 10 mgs. of Zn, of the best ferrocyanide (the author used Merck's) per liter and allow it to stand for a month or more in the dark in a closed vessel. For immediate use one can add 300 mgs. of ferricyanide per liter to the above mentioned solution, but this solution will change in value for some time until all the oxygen dissolved in the water is used up in converting the ferrocyanide to ferricyanide. In standardizing, and when titrating dissolved zinc sulphide precipitates that contain less than 0.3 mgs. of ferrous iron, three or four tenths of a c.c. of ferrous iron solution are added, 1 c.c. of which is equal to a milligram of iron. A ferrous solution may be permanently maintained by acidifying it and adding a few granules of aluminum powder. After much experience with the old end point and observation of others working with it, the author is of the opinion that the new end point is both quicker to reach and more accurate, and he recommends every chemist working on zinc analysis to give it a fair trial. Below are given some factor determinations on various ferrocyanide solutions. In every case the zinc, after being weighed out, was only marked by letter, so as to eliminate mental bias as much as possible.

	1.0665	.5293	.5030
	1.0660	.5293	.5033
	1.0660	.5299	.5035
	1.0665		
Mean	1.0663	.5295	.5033

Below are a series of factor determinations in which the beaker marks were changed and the results calculated by another person, so as to eliminate the personal equation as much as possible.

	.9939
	.9929
	.9932
	.9929
	.9929
Mean	.9932

OTHER VOLUMETRIC METHODS

Of the numerous other volumetric methods proposed, the same thing may be said as of the uncommon gravimetric methods. Their use has never extended far beyond the hands of their originators.

ELECTROLYTIC METHODS

These are divided into two classes. The one working in an alkaline electrolyte and the other in an electrolyte made slightly acid with one of the weaker organic acids, and containing enough alkali salt of the organic acid to prevent any considerable rise in the concentration of hydrogen ions when the zinc is precipitated.

Spitzer[1] has shown that a simple sodium hydroxide electrolyte gives more satisfactory results than any obtained with the complex mixtures. Using two to five hundred milligrams of zinc, the author was unable to get as accurate results as those of Spitzer, but always came from one to two milligrams high. This was undoubtedly due to presence of zinc oxide or hydroxide, as explained by Spear, Wells, and Dyer (J. American Chem. Soc. 32 (1910) page 530–38).

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[1] Spitzer (Zeitschft. f.–Elektrochemie 11 (1905) 391.

With the organic electrolyte, sodium acetate and acetic acid, the author was able to get better results both as to appearance and actual accuracy. The oxide or hydroxide carried down amounting to less than one milligram for from 200 to 500 milligrams of zinc. As in the alkaline method, Spitzer's directions were followed in every detail, he having investigated the electrolytic precipitation of zinc more thoroughly than any one previous.

On the whole, the electrolytic methods, on account of the special apparatus needed, the experience and care necessary to get reliable results, and the unavoidable errors involved in their use, are less desirable than the gravimetric oxide method and still less desirable than the ferrocyanide method, both on the grounds of time required and the difficulty of maintaining the proper conditions.

After summing up the results of the various methods of determining zinc in pure solution the author concludes that the two volumetric titrations, the weighing as zinc sulphate, as oxide and the precipitation electrolytically from an acetic acid electrolyte are the only methods worthy of consideration by the analyst today.

Of these, the ferrocyanide method in the author's hands proved the most accurate as well as the easiest to maintain under proper conditions. Next to this, the author prefers the weighing as zinc oxide. The weighing as sulphate is just as accurate as the weighing as oxide, but takes more time. The Schaffner sulphide titration is probably as accurate as either of the gravimetric methods, but is undoubtedly, from published results by those most familiar with it, less accurate and more time consuming than the ferrocyanide method. The electrolytic method is the least desirable of those worthy of consideration.

One fact well worth considering is the enormous advantage the two volumetric methods have, in that one can run them in the presence of numerous other elements, whereas the gravimetric methods require pure solutions and the electrolytic, freedom from all but a limited number of impurities. For a standard method, this fact has no weight, since, as will be shown later, it is necessary to separate zinc from all the other metals. For individual ores, however, and standardized, rapid procedures, no interfering metal being present or the influence of such being known and allowed for, the fact that the volumetric methods can be worked in the presence of numerous other metals has made them almost universally used.

METHODS OF SEPARATING ZINC FROM OTHER ELEMENTS

Separation from Silica

The separation of zinc from silica, either partially by hydrochloric acid or completely by sulphuric acid, worked satisfactorily for the author. The filtering and washing, when sulphuric acid is used, is decidedly the more rapid procedure and is used almost exclusively on the continent, according to Nissenson.

The separation of the metals of the hydrogen sulphide group from zinc will be given in a little more detail than was allowed in the case of the determination of zinc in pure solution since several new points were brought out here, which require explicit directions and recorded experimental data.

METHOD OF SEPARATION OF CADMIUM, LEAD, ARSENIC, ANTIMONY, AND BISMUTH, FROM ZINC

The literature upon the subject of the separation of zinc from cadmium and the heavy metals is particularly extensive and more or less confusing,—cadmium being apparently the cause of the greatest difficulty.

From the great mass of material worked over, three methods stand out as worthy of first consideration on the grounds of accuracy and simplicity. They are the Thio-sulphate and Hydrogen Sulphide method, used in the German laboratories

((Nissenson u. B. Neumann, Chemk. Zeit. 19 (1895) 1624; Nissenson u. Kettembeil, Chemk. Zeit. 29 (1905) 951)); Waring and Stone method, ((J. A. C. S. 26 (1904) #1, p. 25)); and the Electrolytic method of Denso and Foerster ((Zeit. fur Elect. 9 (1903) 470; Zeit fur Angew. Chem. 19 (1906) 1890)).

Most of the other methods not considered here belong in two classes: those separations which are incomplete, or which careful work has shown to be unreliable; and those in which the zinc solution is left in a condition unsuited for the zinc determination itself. In the first class are included such methods as are used in the Von Schulz and Low Method (Columbia School of Mines Quarterly Vol. XIV #1), where metallic lead is used to precipitate copper, lead, of course, going into solution; also, Low's own methods (Tech. Meth. Ore Anal.) of separating cadmium by hydrogen sulphide in cold solution of insufficient acidity. In the second class would come most of the electrolytic methods, where complex salt solutions are used, as well as the methods based on the difference of solubility of the sulphides of zinc and cadmium in potassium cyanide solution.

Waring and Stone Method

Of the three methods selected, that of Waring and Stone appeared the simplest and neatest and was, therefore, tried first. The method consists in boiling the 10–15% acid sulphate solution of the metals with a heavy piece of sheet aluminum, ¾″ square, until precipitation ceases, then filtering off the solution containing the zinc and metals of the groups beyond. A couple of pieces of aluminum are also put on the filter.

Separate sulphate solutions of bismuth, antimony, arsenic, copper, lead and cadmium, in quantity likely to be met with in zinciferous products, were first tested. Bismuth, antimony and lead were readily precipitated in from fifteen minutes to a half hour. Copper and arsenic, however, went partially back into solution when exposed to the oxygen of the air on the filter during the washing. A dozen trials with cadmium yielded varying results—from a small fraction up to two thirds of the cadmium present being precipitated, using quantities of from two to ten mgs. and boiling as long as several hours.

The presence of six or eight pieces of aluminum, instead of one, thus having more surface of contact for the precipitated metals, and cooling the solution down before filtering, almost entirely prevented the resolution of the copper and arsenic (less than a milligram going through). In the case of cadmium, however, about the same amounts went through as before. A second precipitation of cadmium failed to remove, if any, but a trace of that left by the first operation.

As the separation is really electrolytic, the conditions under which zinc and cadmium are separated by the regular electrolytic methods were studied. According to P. Denso (Zeit. fur Electrochemie 9, 1903, p. 470), F. Foerster (Zeit. fur Angew. Chemie 19, 1906, p. 1890), and others, cadmium can be precipitated and separated from zinc in as strong sulphuric acid as a twice normal solution,—that is, a ten percent H_2SO_4 solution. With a higher degree of acidity, Denso found it impossible to get all the cadmium out. This means that in solutions above ten percent acid aluminum will only displace hydrogen and not cadmium after the latter has reached a definite minimum concentration. It is, therefore, necessary to work below ten percent acid when seeking to precipitate cadmium by aluminum. Furthermore, in the course of the experiments carried out on the electrolytic precipitation of cadmium by the writer it was found that whenever the potential between the electrodes dropped down a little below the point (2.8–2.9 volts) where the precipitation is complete, that cadmium went readily back into solution. This means that as soon as cadmium becomes detached from the aluminum; i.e., is no longer under a strong negative potential with respect to the solution, it will dissolve again in the sulphuric acid. The precipitation can not, therefore, be complete unless all the cadmium remains in contact with the aluminum.

Very large surfaces of aluminum were tried instead of 6–8 squares, but, although the solution was not boiled, part of the spongy cadmium always dropped off the aluminum and when washing was attempted went back into solution, especially when exposed to the air.

A sheet platinum electrode was then tried. This was rested upon a piece of aluminum in the bottom of the beaker of solution.

Sulphate solutions of copper and cadmium were made about 0.5% acid with H_2SO_4 and kept at about 85°–95° for an hour or more. Copper precipitated out first on the electrode beautifully, then the cadmium came down, also in a fine metallic layer completely covering the copper. It was noticed, though, that some of the cadmium adhered to the aluminum. The platinum electrode, coated with copper and cadmium, was removed and cleansed at the same time by washing it with a stream from a wash bottle. When it was attempted to withdraw the aluminum and wash it, the cadmium peeled off. On weighing the electrode it was found that all the copper and about three and a half milligrams of cadmium out of five had been precipitated on the platinum. The solution was filtered immediately, but on testing about a milligram of cadmium was found still in solution.

A platinum gauze electrode was then tried under the same conditions,—the assumption being that, owing to the greater degree of circulation possible with that class of electrode, practically all the cadmium would be precipitated on the platinum and only a negligible portion on the aluminum. No better results were obtained, however, as here, too, some cadmium separated on the aluminum and peeled off and went back into solution during filtering and washing.

These experiments, coupled with the statements of Denso and others, show conclusively that cadmium can not be precipitated and washed free from zinc by simply boiling with aluminum in 10%–15% H_2SO_4 solution and then filtering.

All cadmium can be precipitated by boiling a very slightly acid sulphate solution (less than 0.03% acid) with aluminum, filtering and washing with cold water, but zinc invariably comes down too. A number of experiments were tried varying the acidity near this point, as well as the time, but whenever all cadmium was down zinc was also precipitated in variable quantities up to 5 mgs. Antimony, bismuth, arsenic, copper and lead, however, in quantities likely to be met with in an analysis of zinciferous material, can be satisfactorily and neatly separated from zinc in sulphate solution by boiling for a half hour with a half dozen or more pieces of aluminum,—the solution being made best between 0.5% and 1.0% acid with sulphuric and filtered and washed cold on a filter containing several more pieces of aluminum.

The advantages of this method of separating the heavy metals from zinc are simplicity, and the fact that the solution is in the best condition for the further separating of the zinc from the remaining metals.

The Electrolytic Method of Denso and Foerster

The electrolytic method of Denso and Foerster is only for the separation of cadmium from zinc and the metals beyond, and must be used in conjunction with a method that will first separate the heavy metals. The description of the method by Foerster ((Zeit. fur Angew. Chem. 19 (1906) 1890)) is as follows:

"The 1–2 normal sulphuric acid solution of 100–200 mgs. cadmium is electrolyzed for two to three hours with 0.4 to 0.5 amp., using a coppered or silvered Winkler platinum gauze electrode (surface area 50 sq. cm.). The washing is done without interrupting the current, the cathode washed off with alcohol and the latter carefully dried over a flame.

"If zinc is present in equal or smaller amounts with the cadmium, this, heretofore, very difficult separation is effected by first electrolyzing with 0.1 amp. for five to six hours, and then finally one hour at 0.5 amp., when the cadmium will be completely precipitated and separated from the zinc."

Since the amount of cadmium to be separated in a regular zinc analysis is usually less than 6 mgs. or .6% on a gram sample, it seemed at a glance that this could be separated in one hour at 0.5 amp.

The platinum gauze electrode at hand (surface area 75 sq. cm.) was coppered according to Denso as follows: About 250 mgs. of copper sulphate in 100 cc of solution was heated nearly to boiling, two c.c. of 1:1 H_2SO_4 added, and then the solution electrolyzed at about two volts. In a half hour or less the cathode was coated with a fine hard plate of Cu. The electrode was washed, dried and weighed in the usual manner and was then ready for a cadmium precipitation. During the course of the work, however, it was found best to coat this copper precipitate with one of cadmium also. The completeness of the precipitation of cadmium depends upon the copper being completely covered with cadmium, i.e., a cadmium electrode. The reason is that hydrogen is liberated from H_2SO_4 at a lower potential on a copper electrode than on a cadmium one. This potential on the copper electrode is lower than that required to decompose the last traces of $Cd\ SO_4$, whereas on the cadmium electrode this potential is above that required to precipitate the last of the cadmium. As a consequence, if the copper is not completely covered, hydrogen will be evolved upon it instead of the last of the cadmium. With small amounts of cadmium, like 5 mgs., the copper is not completely covered. To plate the copper electrode with cadmium also, instead of washing and weighing the coppered electrode, simply remove the copper sulphate solution after the regular copper plating, substitute a beaker of cadmium sulphate, about 100 mgs., made 5%–10% acid and electrolyze for a half hour or so at 0.8–1.0 amp. This double plated electrode is washed, dried and weighed and is then ready for the precipitation of small amounts of cadmium. The electrode is used over and over again without re-plating.

After numerous experiments to get the method running smoothly, the following series was run. The cadmium was measured out from a standard solution and an error of about 0.3 mgs. must be allowed for this as well as about 0.2 mgs. for the two weighings of the electrode.

CD Taken	Metals in sol.	Amp.	Volts	Time	Free acid in 120 cc	CD Found	Error
Mgs.	Mgs.				Gms.	Mgs.	Mgs.
3.3	Zn 325	0.95	2.95 – 3.05	1 hr.	7	2.7	–0.6
2.2	" 325	0.95	2.95 – 3.05	1 "	7	1.7	–0.5
11.0	" 300	0.85	2.90 – .95	1 "	6	11.0	.....
3.3	" 300	0.85	2.95 – 3.05	1½ "	6	2.5	–0.8
6.6	" 350	0.95	3.00	1½ "	7½	6.9	+0.3
4.4	" 500	0.95	2.90 – 3.00	1 "	7	3.7	–0.7
6.0	" 500 Fe 50 Mn 10	0.85	2.95 – 3.05	1½ "	7	5.3	–0.6
2.2	Zn 350	0.85	2.90 – 3.00	2 "	6	1.4	–0.8

In only two cases was any cadmium found in the solution after electrolysis and in each case then less than 0.5 mgs. There seems to be a tendency to run a little low, but, as the solution gave no test, except in the two instances mentioned, for cadmium, after electrolysis, the error involved is of the same magnitude as that of the other operations of a regular zinc separation and determination, viz., 0.2 to 0.4 mgs.

In testing the solution for cadmium after electrolysis, it was found impossible by comparison with blanks to detect, by the faint color reaction, less than 0.3 mgs. of cadmium, in 150 c.c. of solution, containing 300 mgs. or more of zinc.

This method of separating cadmium, combined with the aluminum method or the thio-sulphate method for separating the heavy metals, likewise has the advantage of leaving the zinc solution in the best condition for analysis. Another advantage is that, if lead has been removed as sulphate, and arsenic, antimony and bismuth are not present, both copper and cadmium may be precipitated on the same electrode under the same conditions as named above.

Thio-Sulphate and Hydrogen Sulphide Method

The description of the method of separating the heavy metals and cadmium from zinc, as practiced in the German technical laboratories, is as follows ((Nissenson and Kettembeil, Chemk. Zeit. 29 (1905) 951; Nissenson Untersuch. Meth. des Zinks, p. 39, 48)):

The solution of ore or other zinciferous product, is evaporated to the appearance of fumes with 7 c.c. of 1: 2 sulphuric acid and allowed to cool. It is then taken up in about 50 c.c. of hot water. When cadmium is present, hydrogen sulphide is led in, otherwise the solution is boiled with 7 c.c. of 1: 10 sodium thio-sulphate until the evolution of sulphur dioxide ceases, then filtered.

Tests with pure salt solutions showed that the thio-sulphate would precipitate all the heavy metals in the quantity likely to be met with, when the above directions were followed. Cadmium, however, was not precipitated.

It was thought unnecessary to test the precipitation of the heavy metals with hydrogen sulphide. The precipitation of cadmium by hydrogen sulphide in the presence of zinc, however, was made the object of numerous experiments. The following conditions were determined as the best after many variations of all the influencing factors:

The sulphate solution of the two metals (1 to 10 mgs. cadmium, 200 to 500 mgs. zinc) is made 10 to 12% acid with sulphuric acid and hydrogen sulphide allowed to pass through rapidly for fifteen minutes. If, at the end of that time, no precipitate appears, ammonia is added drop by drop until a precipitate does appear. The stream of hydrogen sulphide is allowed to run five minutes longer in the cold solution. The latter is then heated to 70–90° C., the hydrogen sulphide stream still passing through. The solution is immediately filtered and the precipitate is washed several times with cold 8–10% sulphuric acid and finally with hot water. The saturation of the wash acid with H_2S was not found necessary since the resolution of even a large percentage of cadmium would make but a small actual error.

Under these conditions a cadmium sulphide precipitate of 10 mgs. of cadmium (1% on a gram ore sample) in the presence of 500 mgs. of zinc will hold back less than 0.5 mgs. of zinc. Some cadmium will go through too, but numerous tests on pure salts and ores have shown the zinc solution never to contain more than 0.5 mgs. of cadmium after the separation—the two errors about balancing each other.

The cadmium sulphide precipitate has a tendency to run through even the best filter paper, so the latter was first packed by pouring a little dilute ammonium poly-sulphide over it and then a little sulphuric acid and washing.

The use of less acid than will just permit the cadmium sulphide to come down is certain to leave too much zinc occluded in the precipitate. Precipitating and filtering the solution cold likewise greatly increases the amount of occluded zinc.

The precipitation of the heavy metals along with cadmium by hydrogen sulphide necessitates using less acid than will just permit the sulphide to come down, since one is unable in the mixture of sulphides to tell when cadmium has come down. Working with mixtures of various heavy metals, cadmium and zinc salts, the author was never certain whether all the cadmium was precipitated even when the solution was not acid enough to keep less than a couple milligrams of zinc in the precipitate. The experiments with ores, where one has silica present, in addition to the sulphides of the heavy metals, added further weight to the conclusion that cadmium should be separated from zinc by hydrogen sulphide only after first removing silica and the heavy metals. Further evidence in favor of this conclusion is the fact that the heavy metal sulphides can likewise occlude zinc, and, even though one could operate at the highest acidity, the increased mass of precipitate would be sure to hold back too much zinc.

The method then resolves itself into two operations: first, the separation of the heavy metals from zinc and cadmium and the metals beyond; then the separation of cadmium from zinc, etc. Accordingly, one can separate the heavy metals either with aluminum or with thio-sulphate, and then precipitate the cadmium with hydrogen sulphide.

The precipitation of the heavy metals by hydrogen sulphide (previous to separating cadmium) instead of by aluminum or thio-sulphate is not recommended, since both the latter methods are simpler and quicker.

The final separation of cadmium by hydrogen sulphide has one disadvantage as compared with the electrolytic method, viz., the fact that the zinc solution has to be boiled free of hydrogen sulphide, after the separation of cadmium and previous to the separation of zinc from iron, aluminum, etc. The time required, however, is about the same for the two methods.

Conclusion

The method of Waring and Stone, when modified, yields a satisfactory method for separating the heavy metals, but not cadmium.

The electrolytic method of Denso and Foerster gives a satisfactory method for separating copper and cadmium—lead, arsenic, antimony and bismuth being absent or previously removed.

The thio-sulphate method yields a satisfactory separation for the heavy metals. The hydrogen sulphide method for cadmium yields satisfactory results only when the heavy metals have been previously removed.

According to the nature of the impurities in the ore or material, one could take any of the above methods or combination of several of them and get equally satisfactory results. However, in the separation of cadmium by either method, the greatest care should be taken to observe the exact conditions, since slight variations will cause large errors.

As a supplement to this work, the foilowing ore analysis are given:

Four samples of the "D" ore sent out by the Zinc Committee of the American Chemical Society in 1906 were first run as follows:

After solution in hydrochloric and nitric acids and evaporating to the appearance of fumes with 3–4 cc of conc. H_2SO_4, as in the regular procedure, the mass was diluted to about 50 cc; 7 cc of 1: 10 sodium thio-sulphate were added and five or six squares of sheet aluminum; after boiling a half hour to completely decompose the thio-sulphate, the solution was filtered and washed, leaving SiO_2, Pb, As, S, Cu and some Cd. behind; 2 cc of 1 : 1 H_2SO_4 were then added to the filtrate making the latter about 7–8% acid; the solution was then diluted to about 125 cc and electrolyzed with 0.8–1.0 amp. and at 2.95–3.05 volts for one and one half hours. The cathode, anode and cover glasses were then carefully washed into the solution; the cathode washed in three baths of alcohol and carefully ignited. The following increases in weight were found:

6.0 mgs.
4.5 "
5.0 "
5.1 "

Since the ore only contains about 0.6% cadmium, these runs show that practically none of it is precipitated, or remains precipitated, by boiling with aluminum for a half hour, and filtering and washing while hot, even in the presence of thio-sulphate. The cathode was tested for zinc, after the four separations, by digesting a short while in warm 1% H_2SO_4.

This did not remove all the cadmium coating, but, as there was plenty of cadmium in solution the complete solution of the zinc was assured. On acidfying this 100 cc solution with 10 cc of conc. HCl and adding ferrocyanide, not a trace of zinc was found.

The solution containing the zinc was then transferred to a 400 cc beaker, the proper acidity attained, and the zinc precipitated as sulphide, as will be described later. The final determination was made volumetrically.

The following results were obtained on the dry ore:

31.70%
31.68%
31.56%
31.58%

Mean 31.63%

The solutions and precipitates of zinc ferrocyanide after titration were decomposed with nitric and hydrochloric acids and finally evaporated to the appearance of fumes with H_2SO_4; after diluting properly and passing in hydrogen sulphide the mixture of sulphur and cadmium sulphide, if present, was filtered off, this was then dissolved in a little hydrochloric acid and hydrogen sulphide passed into the slightly acid solution. No yellow coloration resulted.

Two samples of the "D" ore were also run in exactly the same way as above excepting that cadmium was precipitated by hydrogen sulphide as follows:

After filtering off the precipitation of Cu, Pb, As, SiO_2, and S, five c.c. of 1 : 1 H_2SO_4 were added, and the solution diluted to 100 cc, making it about 10–12% acid; hydrogen sulphide was then run in rapidly in the cold, for fifteen minutes; at the end of that time, if no precipitate of cadmium sulphide was visible, two or three drops of ammonia were added at a time until the precipitate appeared; after five minutes, the hydrogen sulphide stream continuing, the solution was heated to 70–90° C.; immediately filtered and washed several times with cold 8–10% sulphuric and finally with hot water. The zinc solution was then treated exactly as in the previous cases.

Results:

31.60% Zn
31.63% Zn

Mean 31.62% Zn

$$\left.\begin{array}{l}\text{Mean of 1st series}\\ \text{Cd separated}\\ \text{electrolytically}\end{array}\right\}\ 31.63\%\ \text{Zn}$$

No cadmium was found in the zinc ferrocyanide after titration. The cadmium precipitates on testing for zinc showed 0.2–0.4 mgs. present. The cadmium sulphide precipitate was caught on a filter paper previously packed by pouring over it a little ammonium poly-sulphide and washing out with dilute sulphuric acid. A little cadmium went through at first as evidenced by the faint color of the first part of the filtrate, but that this was not more than 0.3–0.4 mgs., about balancing the zinc held back, was shown by the tests of the zinc solution after titration, which yielded no color; the limit under the conditions named, where cadmium is traceable, is about 0.3–0.4 mgs.

THE SEPARATION OF ZINC, FROM IRON, ALUMINUM AND MANGANESE

But two ways of separating zinc from iron, aluminum and manganese need to be considered. The ammonia and bromine, or ammonia and hydrogen peroxide or persulphate method, which precipitates the three mentioned elements leaving zinc and the metals beyond, like calcium magnesium and the alkalies, in solution, and the hydrogen sulphide method, which precipitates the zinc and leaves all the above mentioned metals in solution.

SEPARATING IRON, MANGANESE AND ALUMINUM WITH AMMONIA

The second method, namely precipitation of iron, manganese, and aluminum by ammonia and bromine or hydrogen peroxide, has been made the object of numerous investigations, all of which lead to the same conclusions, namely, that only with materials low in the above mentioned impurities is it possible, even with two precipitations to keep the retention of zinc by the precipitate below 1 mg. In ores and materials containing up to 5% of iron, less than 0.5% of aluminum and less than 5% of manganese, it is possible, in the presence of ammonium chloride and with careful washing with ammoniacal ammonium chloride, to prevent more than 1 mg. being retained by the precipitate on a half gram sample, but with ores like Franklinite Colorado Concentrates, Broken Hill Concentrates and Japanese Blendes and materials like retort residues, and oxide clinkers, it has been found absolutely impossible to make a satisfactory separation using the ammonia method, even after three or four reprecipitations. The evidence on this point is so varied and extensive that only a few of the more important articles on this subject can be mentioned. The most important articles are by Prosst & Hassreidter (Zeit. fur Angew. Chem. 5 (1892), 166), E. Jensch (Zeit. f. Angew. Chem. 12 (1899), 465), Hampe & Fraatz (Zeit. fur Berg. Hutten and Salinenwesen 25 (1879), 253), Waring (Journ. Amer. Chem. Soc. 26 (1904), 4) and the Report of the Zinc Committee of the American Chemical Society. The evidence given by the above authorities is sufficient to rule out the ammonia method for high iron, manganese and aluminum ores and materials, without adding the authors accumulated evidence of several years' experience with just such ores and materials.

THE SEPARATION OF ZINC AS SULPHIDE

The separation of the zinc, as sulphide, from iron, manganese, etc., has been investigated time and time again. In most cases the directions given for precipitation are very general and indefinite indicating uncertainty in their author's mind. In practically every case, the acidity is too low to prevent considerable iron coming down with the zinc, although the authors claim a good separation. While the writer has not tried all of the various sulphide precipitations, he has tried those made in the most acid solutions, and finds that even when a solution is acid enough to keep 0.5 mgs. of zinc in solution per 200 c.c., as much as 0.5 mg. of iron may be precipitated with the zinc if the zinc and iron are present in about equal quantities.

The Zinc Committee of the American Chemical Society have recommended a modification of Zimmerman's method (Ann. Chem. 199 (1879), 1 u. 204 (1880), 266) of precipitating zinc sulphide. The author, as well as numerous other experimentors, has never been able to get a precipitate, following the directions of this committee, that could be filtered and washed properly in less than an hour's time. Furthermore, the amount of iron retained by such a precipitate varied from 1.5 mgs. to 3.0 mgs., when precipitating 200 mgs. of zinc in the presence of an equal amount of iron. In many cases the precipitate ran through the best grade of filter paper, and in others, the solution washed so slowly that a clean precipitate was impossible. Washing the precipitate with hot water, as recommended in the above mentioned method, was abandoned after one or two trials showed several milligrams to have been carried through by a couple of washings.

Referring to Zimmerman's original articles, the author finds that Zimmerman allowed his precipitate to stand hot for six hours after precipitation. He never precipitated more than 100 mgs. of ZnO in the presence of an equal amount of iron and never tested his precipitates for iron. The author doubts that even after standing six hours, that the precipitate possessed good filtering qualities, since the free hydrogen sulphide in solution would be constantly oxidized to sulphur, which would clog up the pores of the filter. The six hour wait, the uncertainty of the filtering qualities of the sulphide, and the certainty of high iron enclosure on account of low acidity, make the Zimmerman method undesirable as compared to the Weiss method, which will be described later. Nissenson's review, as well as the author's careful review of the many original articles bearing on the sulphide precipitation, leads to the conclusion that G. Weiss (Inaugural Dissertation München 1906) has made the best investigation of the subject. Weiss' work is unusually thorough and leads to logical conclusions and definite directions for making the sulphide precipitation. The following are some of Weiss' conclusions with the present writer's comments on the same:

I—"Sulphate solutions are preferable to chlorides." A $\frac{n}{10}$ chloride solution is not completely precipitated by H_2S. Furthermore, the precipitate of sulphide from HCl solution when quantitative is not crystalline and easy to filter like that obtained from sulphate solution.

II—"The concentration of a sulphate solution is without influence on the completeness of precipitation from $\frac{n}{10}$ down. That is for solutions containing at most 400 mgs. ZnO per 100 cc." In the Modified Waring method 125 mgs. ZnO per 100 cc is set as the limit. In the methods of Hampe, Delfs, Beilstein, Bragard, Von Berg and others confusing and conflicting degrees of limiting concentration are set in a great variety of mixed organic and mineral acids. None of the conditions have been worked out as carefully as those by Weiss and in none are the conditions as simple and as easily maintained.

III—"Sulphate solutions of 400 mgs. ZnO per 100 cc may be $\frac{n}{100}$ acid with H_2SO_4 before beginning to precipitate." Even at acidity $\frac{n}{20}$ before precipitation less than a milligram of Zn remains unprecipitated. This is a much greater degree of acidity than used by Waring or any of the other experimentors mentioned. For example, in the modified Waring method, the precipitation of 300 mgs. of Zn from sulphate solution would be made in 300 cc with the addition of five drops of 20% formic or hydrochloric acid. According to Weiss, if the solution were diluted to 300 cc 1.3 gms. of H_2SO_4 could be added or 6½ cc of 20% H_2SO_4, and still have the precipitation complete. Even if as much as 10 cc of 20% acid were added the loss would still be only a little more than 1.0 mg. Precipitating 300 mgs. from 100 cc., however, only 100 mgs. or ½ cc of 20% acid could be added. This means that when the solution becomes more acid than 550 mgs. of H_2SO_4 per 100 cc the precipitation of ZnS ceases. Knowing approximately the Zn content of a solution one can easily calculate the H_2SO_4, freed when the $ZnSO_4$ that is converted into ZnS, and the difference between 550 mgs. and this calculated H_2SO_4 is the amount of acid that may be added when precipitating from 100 cc of solution. For two hundred cc. of course more acid can be added, being the difference between 1.100 gms. and the calculated H_2SO_4, freed from the $ZnSO_4$. One and one-half times the amount of Zn judged to be present is close enough for the H_2SO_4 freed.

IV—"The precipitation, under the above given conditions, is incomplete when a slow current of hydrogen sulphide is used (about four bubbles per second) one must work with as fast a stream as possible without causing mechanical losses (at least eight bubbles per second)." Weiss is the first one to discuss this all important question in the precipitation of ZnS. His explanation of the efficacy of the rapid stream of H_2S is as follows:

The precipitation takes place according to the following equation:—

$$ZnSO_4+H_2S \rightleftarrows ZnS+H_2SO_4$$

Equilibrium is reached, i. e., the velocity becomes equal in both directions, and precipitation ceases when the amount of H_2SO_4 per 100 cc reaches a certain point, under a given set of conditions. Let these conditions remain exactly the same with the exception of the H_2S and have the active mass of that increased. The equilibrium will be displaced from left to right and as a consequence ZnS will come down in the presence of more acid than before. H_2S is not very soluble in water at room temperature but if one increases the surface of contact between the two the H_2S is dissolved much more rapidly and consequently the mass of H_2S active at any one time greatly increased. This is exactly what is accomplished when the Zn solution is constantly kept full of bubbles of H_2S. One can easily see how greatly increased the mass of H_2S would be in the extreme case, when the solution is all foam. Waring in his original method partially accomplishes the same result, namely, increasing the active mass of H_2S, by working in a closed flask under pressure. He, however, works in very hot solution and at such slight pressure that the effect of the increased solubility due to pressure is outbalanced by the tendency to dissolve less freely owing to the elevated temperature. This is evidenced by the low degree of acidity he is able to work at. In the cold, no doubt, Waring's closed flask, with increased pressure, would enable one to work at as high or higher degree of acidity as with the rapid stream of H_2S but the closed flask is an unnecessary complication when one can use the much more convenient beaker.

V—"A strong current of gas, like that called for above, will precipitate the usual amounts of Zn used in analytical operations in forty minutes."

VI—"At temperatures above 50° the precipitation is incomplete; furthermore, at room temperature the ZnS comes down in a form suitable for filtration."

Weiss found that not only were the precipitations incomplete at high temperatures, but the precipitate was finer and much more difficult to filter. The author has found the greatest difference in good filtering qualities between the precipitates obtained by Waring's method and those obtained by the Weiss method. No Zn was left unprecipitated, however, owing to the dilute solution used in the Waring method.

VII—"Water only is required for washing the precipitates." Weiss only used cold water whereas hot water is recommended in the modified Waring method. The author had to dispense with hot water and use cold after a couple of trials with the Waring precipitates as the hot water and acid always dissolved considerable quantities of Zn.

Working with solutions $\frac{n}{100}$ acid before precipitation and observing the above conditions Weiss precipitated and separated ZnS from varying amounts of nickel beginning at four parts Zn to one part Ni and going up to one part Zn to four parts Ni. Figures are given for every separation indicating an accuracy to within 0.5 mgs. The ZnS precipitate after conversion and weighing as ZnO was dissolved in HCl, neutralized with ammonia and precipitated with colorless sodium sulphide. "The ZnS was always pure white showing it to be free from nickel." From the work the author has done on precipitating Zn from solutions containing iron under the same conditions as Weiss maintained in the case of solutions containing nickel, he is inclined to doubt the complete purity of the ZnS precipitate obtained by Weiss. Working with a solution containing three parts Zn and two parts Fe, between 0.3—0.7 mgs. of Fe came down with a Zn precipitate of 300 mgs. Since nickel sulphide is partially precipitated from neutral mineral salts (Baubigny, Compt. Rend. 1882, 94, 1183; 95, 34), while iron sulphide is not precipitated appreciably from neutral mineral salts, zinc sulphide should bring down or retain more Ni from a Zn–Ni solution than Fe from a Zn–Fe solution. Tests show that 0.5 mgs. of Fe or Ni sulphide will only give a faint grey color to 300 mgs. of Zn as sulphide in a hundred c.c. of solution.

Weiss does not take up the separation of Zn from Fe but the conditions that will separate Zn from Ni are more than sufficient to separate Zn from Fe, for the reason already given. Manganese and aluminum require alkaline solution to produce even the slightest precipitation and are therefore not precipitated with the ZnS even when the solution is kept nearly neutral with sodium acetate. Numerous ZnS precipitates have been tested for these two elements and, if any, only traces found.

With regard to the small amount of iron the author always obtained with the ZnS precipitate, while Weiss obtained no nickel under the same conditions, it may be that the more rapid and more effective washing, possible when filtering on a Gooch as compared with a paper filter and no suction, except that of the column in the funnel neck, prevents some Fe from precipitating as sulphide when the acid solution left on the paper is diluted by the wash water. A similar common phenomenon was first observed by Larsen (Zeitschrift f. Anal. Chem. 17 (1878) 312) in the precipitation of CuS in the presence of Zn. The author has noticed this after precipitation, particularly in the case of the separation of Cd and Zn by means of H_2S where it was found necessary to wash with acid at first rather than water in order to keep ZnS from coming down in the diluted solution on the paper. In the four ores run by the author where the ZnS was washed on a Gooch after Weiss, however, the amount of Fe in the precipitate was no less than that usually found when the filtration and washing was done on paper.

With regard to the completeness of the precipitation of ZnS Weiss' results, by the oxide method, indicate a few tenths of a milligram to be left behind on the average. The author finds this the case too; the mean of some fifty or more second precipitations from neutral solution, the Zn estimated with ferrocyanide, yielding about 0.2–0.3 mgs. as left behind. In no case was more than 0.5 mgs. found.

So much for the precipitation of zinc sulphide. It might be added here that Weiss also tried to determine Zn by precipitating as carbonate and blasting to oxide. He found the precipitate to contain both silica and alkali in quantities up to 5 mgs. and the method therefore unsuited for quantitative work.

SOLUTION OF ORE OR ZINCIFEROUS MATERIAL

The author's work on methods of solution disclosed nothing new, merely verifying the observations of others of the presence of small amounts up to 0.3% of acid insoluble zinc in Franklin Furnace Ores. For most purposes it is unnecessary to determine this acid insoluble zinc, but if it is desired it can readily be determined by evaporating the acid insoluble residue with hydrofluoric acid and then fusing with acid potassium sulphate. The acid insoluble zinc is present in a whole series of minerals, the two important ones, however, are Grahnite and Rhodonite. As was remarked under the head of Separation of Zinc From Silica, the author finds that highly siliceous materials can be filtered and washed free from zinc much more rapidly when the silica has been dehydrated with sulphuric acid than when hydrochloric acid is used. As the separation of the heavy metals, cadmium, iron, manganese and aluminum from zinc requires a sulphate solution, all materials that are to be run by the standard method are evaporated to appearance of fumes of sulphuric acid after getting them into solution with hydrochloric acid.

THE PROPOSED STANDARD METHOD IN TOTO

It is fortunate that the best procedure in each of the three fundamental operations of zinc analysis fit together better than any other combination. The proposed standard method in toto consists then in the following combination of the methods selected as being the best for each of the three fundamental operations of a zinc analysis.

One-half gram, in case of materials containing more than 50% zinc, and one gram in case of materials lower than that in zinc, is weighed out into a tall lipless Jena beaker of 150 c.c. capacity, moistened with a little water and 10 c.c. of HCl (1.20 specific gravity) added, slipping a cover glass over immediately. A sample for the moisture determination at 110° is taken at the same time. The sample in which Zn is to be determined is then boiled moderately for a half hour or so on a hot plate. The cover glass is removed, 10 c.c. of 1 : 1 sulphuric acid added, and the whole evaporated slowly to appearance of strong fumes of sulphuric acid. In the case of very silicious materials, it is better to break free the silica adhering to the glass with a stirring rod before adding the sulphuric acid. The solution is then diluted to 40–50 c.c. and about a gram of aluminum powder added. The cover glass is again put on and the whole boiled until water white—(about 10–15 minutes are required). This will reduce the iron and precipitate all the hydrogen sulphide metals except cadmium. The silica and precipitated metals are then filtered off.

One c.c. of 1 : 1 sulphuric acid is then added to the filtrate, in case cadmium is to be removed electrolytically, the solution diluted to 125 cc and then electrolyzed with 0.8–1.0 amp. per 100 sq. cm. electrode area for one and one-half hours at 2.95–3.05 volts.

In case cadmium is to be removed with hydrogen sulphide, 5 c.c. of 1 : 1 sulphuric acid are added, and after diluting to 100 c.c. a rapid stream of hydrogen sulphide is passed through the solution for 15 minutes. Dilute ammonia is then added drop by drop, until the yellow cadmium sulphide starts to come down. The solution is then heated to 70–90° C., continuing the current of hydrogen sulphide, and then filtered through a filter paper previously packed by washing with poly-sulphide, an acid and water. The precipitate is washed with cold 8–10% H_2SO_4, and finally with hot water.

The filtrate is then boiled to remove hydrogen sulphide. A rod of aluminum will help the boiling-off process considerably. The solution is cooled, neutralized with caustic potash and sodium bicarbonate to within an acidity equivalent to a couple of drops of 20% sulphuric acid, and from two to four c.c. of 5% sulphuric acid added, according to the amount of zinc present per 100 c.c. of solution. A rapid stream of hydrogen sulphide is then passed through the solution for forty minutes. After settling ten or fifteen minutes, the zinc sulphide is filtered off and washed with cold water. A hole is punched in the filter paper and the sulphide washed back into the beaker in which it was precipitated. The filter paper and glass tube are then washed into the same beaker with 10 c.c. of HCl in hot water. The resulting solution is boiled for fifteen minutes to remove hydrogen sulphide, 13 c.c. of ammonia (90 sp. gr.) added, this in turn neutralized with 3 c.c. conc. HCl, (1.20 sp. gr.) excess of the latter added, and the whole diluted to 200 c.c.

The ferrocyanide titration has already been described under the head of the determination of zinc in pure solution. The ferrocyanide is standardized with amounts of zinc corresponding very closely to the amount present in the ore sample. The amounts of ammonium chloride and free hydrochloric acid present in the standards should of course be the same as in the ore sample. A ferrocyanide solution 1 c.c. equal to 10 mg. of zinc, has a temperature coefficient sufficient to decrease the factor 0.2% per 5° C. rise in temperature, so care should be taken that no sharp change of temperature between standardization and ore titration occurs without being corrected for. The metallic zinc used for standardization should contain less than 0.03% lead and 0.02% iron and less than two hundredths percent of other impurities. The surface should be scraped clean of oxide before cutting. Merck's and Kahlbaum's best grade of stick zinc both meet these requirements as does Baker and Adamson's and Eimer and Amend's powdered zinc. The powdered zinc, however, has to be examined very carefully before weighing, as it invariably contains foreign material as well as granules that are oxidized to a visible extent.

The standard method is considerably shortened when cadmium is absent or present in quantities less than 0.05%. If an ore runs very uniform in cadmium, as many ores do, a constant deduction may be made for it after having once determined its influence, instead of separating it as a regular procedure.

In concluding this paper, the author wishes to state that he realizes that there are faults to be found with the method, but urges every chemist doing zinc analysis to give it a trial and report their results, remembering always that the method is designed as a check on the rapid methods, which can be gotten up for each class of ores, after one becomes familiar with their possible variations in constitution, and is not intended as a substitute for these rapid methods in regular routine work.

A NEW METHOD FOR THE ANALYTICAL AND QUANTITATIVE SEPARATION OF MERCURY FROM BISMUTH

PROF. ADOLFO P. CASTAÑARES
Mexico City

The separation and quantitative determination of Mercury and Bismuth can be easily made, and with great precision, if notice be taken of the fact that mercuric compounds, when hot, are not precipitated by ammonium carbonate, provided that the solution used be highly acidified with nitric acid; whilst, under the said conditions, the Bismuth is totally precipitated.

From the experiments I have made, it appears that the best conditions for obtaining a complete separation are found when the concentration of the mercury in the solution does not materially exceed 0.1 gramme per cent.

The following is the technique of the operation: First the solution containing mercury and bismuth is acidified with concentrated nitric acid (D. 1.42), 5 cubic centimetres of the latter being added for every 100 c.c. of the solution. The resulting mixture is heated in a water-bath up to about 60° C. Then a 10 per cent solution of ammonium carbonate, containing 1 per cent of ammonia, is added, this being done slowly and carefully in view of the evolution of $CO2$, until a decidedly alkaline reaction occurs. The temperature is raised to 80° C., and is maintained by frequent stirring until no more $CO2$ is expelled. The precipitate is allowed to settle and is filtered off.

If the solution only contains the two metals in the state of a nitrate, it can be filtered off directly in a Gooch crucible, previously brought to red heat, the precipitate being washed with a 1 per cent solution of ammonia (D. 0.90). The precipitate, formed of basic nitrate and carbonate of bismuth, is dried at a temperature of 100° C. and is then repeatedly heated to red heat to constant weight. From the weight of the $Bi2O3$ obtained is deducted the amount of bismuth. When the solution contains chlorides, the precipitate obtained by the carbonate has to be filtered, dissolved in dilute nitric acid and evaporated. The residue has to be treated three or four times with concentrated nitric acid, being evaporated each time in a water-bath (for then, as has already been stated by several writers on the subject, the precipitate contains oxychloride of bismuth, which, on being brought to red heat, is subject to losses on account of its volatility), so that it may be transformed into nitrates and precipitated in that form by carbonate of ammonium, or by phosphate of ammonium, the latter being the method I have preferred, following the suggestions of L. Moser (Zeitschr. f. Anal. 45, (1906) 19).

In both cases, the filtered liquid, which results from the treatment of the solution with ammonium carbonate and contains all the mercury in solution, is warmed, treated with a slight excess of freshly prepared sulphide of ammonium, boiled for a few minutes, left to settle and is then filtered in a Gooch crucible heated up to 100° to 110° C., it is washed with water containing sulphide of ammonium in solution, then again with absolute alcohol, and is dried at a temperature of from 100 to 110° C. Under these conditions, the HgS obtained is free from sulphur and no further treatment with carbon bisulphide is necessary.

For the purposes of my investigations I prepared two solutions one of HgC12 (chemically pure) in distilled water and the other of bismuth (Bismutum purissimum) in nitric acid, and carefully tested both.

The following were the results obtained on analyzing mixtures (in varying proportions) of both solutions:—

HgS		Bi	
Calculated	Found	Calculated	Found
0.1244 grs.	0.1242 grs.	0.1350 grs.	0.1351 grs.
0.1244 "	0.1240 "	0.1404 "	0.1406 "
0.1295 "	0.1294 "	0.1458 "	0.1458 "
0.1343 "	0.1338 "	0.1350 "	0.1347 "
0.1443 "	0.1445 "	0.1566 "	0.1570 "
0.1492 "	0.1489 "	0.1620 "	0.1623 "
0.1492 "	0.1491 "	0.1566 "	0.1565 "
0.1393 "	0.1389 "	0.1620 "	0.1627 "

The method, as can be readily observed, in addition to its simplicity and rapidity, possesses the advantage of being very precise, a quality worthy of being taken into consideration.

REPORT OF THE SUB-COMMITTEE ON STANDARDISATION OF METHODS ON DETERMINING WATER IN COALS AND OTHER FUELS AND IN MINERALS OF THE INTERNATIONAL COMMITTEE ON ANALYSES

PRESENTED BY

R. LESSING, PH.D.[1]

President of Sub-Committee: G. T. HOLLOWAY (England); Vice-President: J. H. COSTE (England); Members: HUYBRECHTS, DE KONINCK (Belgium); STANSFIELD (Canada); ANDREWS, BANNISTER, BURGESS, CLOWES, HILLS, HODGKINSON, HUNTLY, LESSING, POLLARD, POWNEY, ROSENHAIN, SEYLER, STEAD (England); COHADE, LACOMBE, NICOLARDOT (France); T. W. FRESENIUS (Germany); BAUCKE (Holland); CONSTAM (Switzerland); JOHNSTON (Transvaal); BASKERVILLE, HILLEBRAND, PRAGER (United States).

The purview of the committee as defined in a circular letter issued by the President in March, 1911, includes the consideration of:

1) The determination of moisture and of combined water, including water of hydration and of crystallization.

2) The limits of accuracy possible or desirable in general or special cases.

3) The errors which would be introduced into other portions of an analysis by the use of a defective method of water determination as for instance, in the case of fuels, where combined

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(1) This Report has been written by the President and Vice-President who have consulted such Members of the Sub-Committee as were available. It was obviously impossible for the whole Sub-Committee to meet but, in framing the Report, every endeavour has been made to give due weight to the suggestions and work of those Members who have communicated with the reporters.

water other than that actually determined, would frequently be calculated out as hydrogen.

4) Methods of general application or suitable only to special cases or types of fuel or mineral, such as the effect of the use, and limitations of the use, of so-called inert gases, absorbents, vacuum drying, etc.

Indirect methods, such as the liberation of hydrogen by the action of the water on calcium carbide, etc., may be considered under this heading.

5) Methods of sampling, storing and of generally dealing with the material to be examined, so that errors other than those due to the method of analysis shall be minimized. This is important in all cases, but especially in connection with coal and coke.

The following extract from the same letter usefully supplements the above summary:

"It must be remembered that the term 'water' includes water in any form, free or combined, and not moisture only, and that, although the methods of determining water in mineral substances and in fuel, are in many cases similar, the conditions and requirements often differ considerably.

"It may therefore prove advisable to consider the committee as being divided roughly into two sections, one for fuel and one for minerals, although they will work in conjunction and will furnish a joint report, possibly divided into sections. Such members as are specially interested in either branch may therefore, should they think best, devote their attention mainly to such branch, although their opinions are solicited also in connection with the other branch.

"The determination of water is much more difficult, and its technical and scientific importance is far greater than appears at first glance. In fuel, its bearing on the determination of hydrogen is extremely important, as the combustion method, in which the water produced is calculated out as hydrogen, is commonly employed and is often used in calculating out calorific values, etc.

"It would probably be correct to state that no really accurate determination of hydrogen in coal has yet been made, on account of the presence of combined water in the mineral constituents which ultimately, after being de-hydrated constitute the ash.

"In the case of minerals, instances frequently occur where generally accepted and apparently correct methods of determining water prove to be inapplicable or to require substantial modification.

"It is proposed that the report of the committee shall include, not merely suggestions as to standard or special methods, but general recommendations as to difficulties which are still unsurmounted and, so far as possible, suggestions as to researches still remaining to be carried out."

It has not been found possible to cover the whole ground of the reference to the committee since, owing to the fact that members have many other onerous duties to perform, the amount of active experimental work done has been limited. Nevertheless, a great deal of useful work has been done on one most important branch of the subject, the determination of water in coal, and many useful suggestions on other matters have been received. It is felt that the hope expressed in the President's circular that" The Committee's Report should thus possess a value beyond that belonging to a mere statement of the results obtained by its members as, in addition to suggesting standard methods of conducting determinations of water and reporting results, it should provide members of the profession with the keynote for further research" has, to a not inconsiderable extent, been fulfilled.

Owing to the great preponderance of the work on Coal, it has been found necessary to confine the report to the consideration of Fuel, although much is directly applicable to minerals, and it is hoped that the members and others will not only continue their work on fuel, but will carry out researches in connection with minerals on the above and other lines. The suggestions which have been received regarding minerals have been too few and too scattered for inclusion in this report, but show the desirability of continuing the work and of the issue of another report relating especially to minerals or the publication of individual papers dealing with that most important subject.

The work done has convinced those who have drawn up the report that the recommendations embodied in it can only be considered as of a tentative character and by no means as indicating anything like finality.

The distinction, by analytical methods, between water present as "moisture," "water of combination" and "water of crystallization" offers great difficulty in view of the varying conditions under which different substances part with water present in the two latter forms, and of the fact that the amount of water present in the somewhat indefinite form of moisture appears to be fairly sharply defined by the nature of the substance with which it is associated and the atmospheric conditions prevailing at the time.

I

THE DETERMINATION OF WATER IN COAL

On the suggestion of several members of the committee a series of six samples of coal marked 1 to 6, ranging from an anthracite to a coal containing over 12% of sulphur, were sent to members who were able to do experimental work for this report. They did not cover the range which had been desired; but shortness of time rendered it necessary to send what was available.

The samples sent out were prepared as follows:

A quantity of the coal was ground in a Krupp ball-mill and sifted through the 100 mesh standard 1 mm. sieve having 1–200th inch apertures. The coal thus prepared was left exposed for some days in shallow trays so as to be thoroughly air dried under atmospheric conditions. Lots of about 200 grams of each sample were tinned off, 30 tins of each sample being charged and sealed at the same time. At uniform intervals during such charging, small glass tube samples were taken and immediately sealed with the blowpipe. Twelve such tubes were taken from each of the six samples and some of them have been kept as reference samples; the remainder have been tested as described in Section 5 of this part of the report.

The lever top tins had been previously tested and found to be practically but not absolutely air tight. The lids, after being forced into place, were therefore sealed by means of rubber solution which has been proved harmless and effective, and safer and better than soldering. The samples sent out to each member of the committee may be relied upon as being identical, and as truly representative of the air-dried coals.

Many different types of grinder, in addition to the ball-mill, were tried, including the ordinary coffee-mill type and disc grinders, but the ball-mill was actually employed, as less loss of water was experienced. Even though three large disc grinders were used, two cooling while the other was in use, considerable loss of water occurred, and no method of grinding, except in a sealed vessel, appears to overcome this objection. This point was brought out in the report of the American Chemical Society Committee.

The following table shows the approximate amounts of moisture, volatile matter and ash in the samples:

Sample number	1	2	3	4	5	6
	%	%	%	%	%	%
Moisture	3	10	8	6	7	8
Total volatile matter ex water	5	35	34	23	33	27
				(Ex Sulphur)		
Ash	8	3½	4½	37	8½	10

These figures are extremely rough and are merely given as an indication of the type of coal.

N° 1 is an anthracite from South Wales.

N° 2 is from the "10 yard" or "thick coal" seam of South Staffordshire (England), which, in many respects, resembles a lignite and which extends under the whole of South Staffordshire. It has never yet been coked in practice. As mined, it contained 10 or 11% of water, 5% of hydrogen and 13% of oxygen.

N° 3 is from the Kilburn seam of Leicestershire (England) and is a coking coal largely used for general and household purposes.

N° 4 is a coal from South America, and is interesting in connection with moisture determination on account of its high content (4,2% volatile and 8,2% non volatile). No pyrite is visible or can be washed out, but the coal rapidly weathers and

TABLE 1A. RESULTS SHOWING PERCENTAGE LOST BY COAL WHEN HEATED AT 104°–107° C. FOR ONE HOUR.

Worker	Particulars of Method			Coal Number					
	Grams of Coal	Weighed in	Heated in	1	2	3	4	5	6
I	1	Platinum crucible.	Wiesnegg oven.	2,80	9,50	7,00	5,10	6,90	7,10
II	1	Porcelain crucible.	Electrically heated oven, 100–105°.	2,92	9,76	7,49	5,53	7,30	7,80
				2,86	9,58	7,31	5,65	7,26	8.04
			Electrically heated oven, 100–105°.	3,05	10,25	8,00	6,05	7,68	8,01
				3,13	9,99	7,98	5,98	7,44	8,16
III		Porcelain crucible.	Oven with air circulation at 105°.	2,87	9,86	6,98	5,86	7,14	7,43
				2,92	9,76	6,90	5,83	7,21	7,48
IV	1	Porcelain crucible.	Toluene oven.	3,11	10,06	7,74	6,08	7,56	7,66
V	1	Platinum crucible.	Thermostat at 105°.	2,75	9,63	7,37	5,77	7,09	7,31
VI	1	Watch glasses.	Toluene oven.	3,15	9,59	7,47	5,38	7,38	7,56
VII	1	Shallow stoppered weighing bottles.	Toluene oven with air current.	2,96 2,98 } 2,97	10,16 10,16 } 10,16	7,54 7,64 } 7,59	6,04 5,95 } 5,98	7,63 7,64 } 7,64	7,91 7,98 } 7,95
VIII	1	Porcelain crucible, weighed covered.	Air bath with 2 thermometers, 105°.	3,22	9,72	6,52	5,88	7,14	7,10
				2,72	9,18	6,66	5,28	6,56	6,92
	1	Weighing bottle.	Air bath with 2 thermometers, 105°.	3,06	9,82	7,34	6,04	7,24	7,53
				3,24	9,92	7,46	6,24	7,32	7,46
X	1	Porcelain crucible.	Air bath with 2 thermometers, 105°.	3,16	10,16	7,79	6,19	7,34	7,45
XI	1	Berlin porcelain crucible 00	V. Meyer Toluene bath.	2,90	9,83	7,17	5,67	7,03	7,22
	1	Watch glasses.		2,95	9,86	7,34	5,95	7,28	7,45
XII	1	Nickel boat weighed in tube.	Air bath with current of dry air.	3,19	10,22	7,52	6,42	7,47	7,92
XIII	1	Porcelain crucible with lid 40 mm. at top.	D'Arsonval oven with glycerine bath, with Roux bimetallic regulator 105°.	2,96	10,16	7,30	5,86	7,20	7,36
XIV	1	Porcelain crucible with lid.	Oven at 105°.	2,86 2,78 2,72 } 2,79	9.80 9,79 9,75 } 9,77	7,19 7,07 7,13 } 7,13	6,00 5,99 6,00 } 6,00	7,05 6,99 6,22 } 6,99	7,11 7,23 7,05 } 7,13
XV	1	As officially described.		2,89 2,94 } 2,92	9,92 9,87 } 9,90	7,47 7,45 } 7,46	6,06 6,03 } 6,05	7,31 7,31 } 7,31	7,49 7,40 } 7,45
XVI	1	As officially described.	Toluene bath.	2,72	9,40	8,96	5,15	6,78	6,80
		MAXIMUM		3,24	10,25	8,00	6,42	7,63	8,16
		MINIMUM		2,72	9,48	6,52	5,10	6,22	6,92
		AVERAGE		2,96	9,84	7,33	5,84	7,20	7,48

develops free H^2So^4 and $FeSO^4$. It contains 35% C and 3%H and has a calorific value of about 7,000 B. T. U. Its ash contains about 47% Fe^2O^3, 17% Al^2O^3, 35% SiO^2, only 0,72 % S and less than 0,5% of CaO or HgO. As might be expected, it clinkers badly, but it is used locally owing to high cost of imported coal.

N° 5 is an ordinary bituminous coal from Leicestershire.

N° 6 is a somewhat less bituminous coal from the Southeast of Scotland.

Members of the Sub-Committee were asked to determine the moisture in the coals sent to them:

1. By the "American Standard" method:
    a) Heating for 1 hour in a toluene or similar bath.
    b) Heating for 2 hours in a toluene or similar bath.
2. By the method ordinarily employed by them.
3. By a vacuum method if 2 be not a vacuum method.
    (See sections of this report 1–3).

Several members experimented with other methods, which in this report are included under section 4.

The results obtained by members using the various methods follow under the sectional headings indicated above. A list of the members who undertook this work is appended.

The best thanks of the reporters are due to these gentlemen who by their efforts have assisted in advancing the important question at issue at least a few steps nearer a final solution.

The Roman numeral after a name indicates the results in the tables for which the member or members may be responsible.

E. R. Andrews	XII
C. O. Banister	XVI
H. Baucke	III
W. T. Burgess	X
Staff of Messrs. Schneider and C°, Le Creusot	XIII
E. J. Constam	XV
J. H. Coste	XII
H. F. Hills	IV
G. N. Huntly	VII
M. Huybrechts	XIV

A. Mc. Arthur Johnston	IX
L. L. de Koninck	XIV (1)
G. Lacombe	I
R. Lessing	VIII
C. Nicolardot	II
W. Pollard	XI (2)
W. E. F. Powney	XII (3)
Prager	—
W. Rosenhain	V
C. A. Seyler	VI

1A

STANDARD AMERICAN METHOD

The following method for the determination of moisture in coal is taken from a report of the committee of the American Chemical Society on Coal Analysis (W. A. Noyes, W.-F. Hillebrand, C. B. Dudley), J. Am. Chem. Soc. 1899, XXI, 1116–32.

One gramme of the coal is dried in an open porcelain or platinum crucible at 104° to 107° C. for one hour, preferably in a double-walled bath containing pure toluene, although any bath giving the necessary temperature may be employed. Cool in a desiccator and weigh covered. Longer heating is undesirable, as oxidation and increase in weight occur. A higher temperature is not advisable, although the results obtained when using a Xylene bath (138° C.) indicate that variations of several degrees in the temperature of the bath if sufficiently above the boiling point of water have no effect.

This method is entitled to serious respect as the outcome of a considerable amount of work by the above committee. It is probably very largely, but by no means universally, used. This is shown by the fact that several Members of the present Sub-Committee do not ordinarily use this method or any modification of it.

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[1] (2 names) Worked together.

[2] Assisted by Mr. E. G. Radley. Results published by permission of the Director of H. M. Geographical Survey.

[3] (3 names) Worked together.

We have indicated in the table the various arrangements used by workers. This information we supplement by a few more detailed notes.

I.—The Wiesnegg oven is an inner porcelain vessel heated by tube burners and contained in an outer cast bronze vessel, between which and the porcelain the products of combustion escape.

II.—The electrically heated oven had triple walls and was heated by means of a nickel-iron coil outside the drying vessel. A thermometer, placed with the bulb on a level with the vessels used to hold the coal, did not vary day or night. It remained at 105° C. The double walled gas heated oven used by this worker for some of his experiments did not vary in temperature by 1-10°. The supply of gas was regulated by a governor.

V.—The thermostat was heated by steam under such a pressure as to secure a temperature of 105°. The results shown are mean of closely agreeing duplicates.

VII.—Weighings corrected for errors of weights but not reduced to vacuum. Duplicate estimations separately sampled down from bulk. Bottles cooled in desiccator over fresh H^2SO^4.

VIII.—Crucibles and closed bottles cooled in calcium chloride desiccator.

X.—Upper part of bath protected by flannel cover. Crucibles placed on perforated shelf under which were two other copper shelves, close but not in contact.

XII.—Tube air bath described Jour. Soc. Chem. Ind. 1896, XV, 417. Temperature inside bath within 1° of that registered by thermometer, as indicated by thermo junctions wrapped around thermometer bulb and covered with coal in the nickel boat respectively. Temperature shown by thermometer constant to 1°.

An examination of the results obtained by drying for one hour at a temperature of from 104° to 107° shows that these conditions are by no means as strictly defined as is to be desired and that to comply with them is not easy. The observed variations for all the coals are much greater than at first sight might have been expected of so apparently simple a determination as that of moisture. The differences between maximum and minimum figures for each of the coals are set forth below:

	1	2	3	4	5	6
	%	%	%	%	%	%
	0,52	1,07	1,48	1,32	1,46	1,24
The averages being	2,97	9,86	7,33	5,86	7,21	7,51

These figures represent variations of from 10% to 22% of the amount of water present. From a practical point of view, however, it may be contended with some reason that it would be fairer to consider these as determinations of dry matter rather than of water. In this case the order of the errors is reduced to between 1 and 2 %. It should certainly be remembered that it is the dry matter that signifies, rather than the water associated with it. This consideration does not affect the errors caused in ultimate analysis by the presence of water in supposed dry coal.

A few sources of error may be considered. In the first place it cannot be contended that an ordinary crucible, either of porcelain or platinum, is a vessel of suitable shape for use in such a determination as that of moisture in any substance; more particularly one as liable to oxidation as coal, which should therefore be dried as quickly as possible. The American Committee, in indicating that platinum crucibles, which are usually of a tall form, give on the whole lower results than porcelain, have hit on a weak point in the method recommended by them.

This point is again brought out in the two series of results of the worker II who, in all cases, obtained higher average results in porcelain than in platinum, and higher individual results in all cases but one (N° 6), this one difference being trifling. The worker V, who used a platinum crucible, in only one case, obtained a result (N° 3: 0,04%) above the average. It is, we think, clear that the aim in determinations of this kind, should be to expose as large a surface of the material to be dried as possible. A crucible is perhaps the worst shaped open vessel for this purpose.

Apart from the objection which we raise to the form of crucibles used as drying vessels, we must point out that coal is a very hygroscopic substance, and that to weigh dry coal in an open or loosely covered vessel is a very risky proceeding.[1] We may here quote usefully from the report of Professors Huybrechts and De Koninck who say of the former's work by this method (XIV).

"The process . . . gave lower results than those furnished by the first process examined" (drying for 15 minutes in a weighing bottle at 105°). "This was prophesied" . . . "The weight of desiccated coal in crucibles (fitted with their lids) is less certain than the weight of these substances in bottles ground in emery, for dry coal is very hydroscopic."

"The three crucibles containing the portions taken from one sample were placed in the same desiccator. At the time of weighing, the first was withdrawn, placed immediately on the pan of the balance and fitted with its lid. The weights of the second and third followed and were taken as quickly as possible. Although the desiccator was only open an instant and the weight was taken very quickly, the absorption of a little moisture from the air took place. This phenomenon was not very marked and perhaps it would have escaped my attention if the second portion had not regularly shown (with two exceptions) a loss of weight *smaller* than the first, the third a loss *smaller* than the second (see table 1 *a*)."

We have averaged all the results in table 1 *a* in which the coal was dried in shallow stoppered weighing bottles, watch glasses ground to fit, or a boat which was weighed in well fitting tubes. The figures are in every case higher than those for the whole series tabulated under 1 *a* as will be seen below:

1	2	3
3,08 ±0,04	9,96 ±0,08	7,47 ±0,04
4	**5**	**6**
6,00 ±0,11	7,42 ±0,06	7,69 ±0,08

the greatest difference between individual results was

0,29	0,63	0,30	1,04	0,40	0,53

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[1] We allude later to the precautions to be observed in handling coal samples in dry climates.

It appears from these results that the inferiority of crucibles, more particularly of platinum crucibles as compared with vessels of glass with closely fitting covers is established.

The temperature of a substance placed in an oven is not always easily ascertainable. More particularly is this the case in an air oven heated by a gas burner or a series of burners. The bottom may be nearly red hot and the top at a relatively low temperature. The falling off of temperature between these positions is affected by the air current which should pass through the oven.

It is therefore a difficult matter to insure that the coal placed in an oven, in some part of which a thermometer indicates a temperature of 105° or thereabouts, is itself actually at that temperature. The effect of small differences of temperature is probably negligible since the American Committee found that boiling Xylene (138°) gave much the same results when used to heat the drying bath, as toluene. Members of this present sub-committee (XII) found that a coal which lost 13,90% at 105° in two identical determinations in one hour in a current of dry nitrogen (containing less than 0,5% of oxygen) lost as much as 12,72% in the same time at only 63°, 13,34% at 79° (after 2 hours 13,59%, after 3 hours 13,69%, after 4 hours 13,69%, then after one hour at 105° 13,95%) 13,55 in a water oven, while the same portion used for the experiments at 79° and 105° gave 13,78% at 130°, a gain due either to traces of water or to oxygen in the nitrogen. The heating in these experiments at 63°, 79°, 105° and 130° was performed in a bath in which the coal was exposed to a constant stream of nitrogen (J. S. C. I., 1896, XV, 417). It appears therefore that, so long as the temperature is at least as high as 105°, no great discrepancy due to this cause is probable, although it is better to aim at the prescribed temperature of 104° to 107°, but from these data, it is clear that temperature below 100° gives results which are almost certain to be low, owing probably not to the impossibility but to slowness of the drying when the greater part of the water has escaped.

1B

STANDARD AMERICAN METHOD, BUT DRYING CONTINUED FOR 2 HOURS

Drying at 104°–107° for 2 hours gave results which, on the average, were lower than those obtained with the same coals dried for one hour. In some cases individual results were higher than those obtained by heating for the shorter period but the weight of evidence was in favor of the view that any extra loss of moisture which may occur is more than balanced by the gain in weight due to oxidation. One worker (III) says: "In my opinion the variations in the results obtained by drying in an open porcelain crucible for one or for two hours are but slight and do not permit certain conclusions": others (VII, VIII, X, XI, XII and XIII) comment on the relative lowness of the two hours' results. In the case of XIV the same phenomenon due to hydroscopicity is noticed as has been already commented on; viz., the progressive lowness of triplicate results due to gain in weight on end opening of the desiccator. One worker (VIII) comments of the gain in weight observed when the one-hour portions are repeated for a second hour. We shall return to the question of the time factor in a later part of the report, in the meantime we emphatically state that *there appears to be no sort of advantage to be obtained by heating coal for a longer period than one hour at a temperature of* 104°–107° *for the determination of moisture.*

Additional details of methods ordinarily used by Members of the Sub-Committee:

II.—To render his results comparable with those obtained at 105° this worker dried in a cast-iron oven with porcelain walls regulated to 110°, instead of (as required by the regulations of 5th February, 1908, for the supply of Mineral Fuel . . . and other regulations) using a water oven which, he remarks, always has a lower temperature than 100°, sometimes much lower.

III.—Method not specifically stated to be that ordinarily employed.

IV.—Method not specifically stated to be that ordinarily employed.

TABLE 1B.

RESULTS SHOWING PERCENTAGE LOST BY COAL WHEN HEATED AT 104°-107° C. FOR TWO HOURS.

Worker	Particulars of Method	Coal Number					
	Weighed in	1	2	3	4	5	6
III		2,60	9,65		5,87	7,21	7,35
		2,54	9,72	6,95	5,91	7,19	7,35
IV		3,02	9,96	7,62	6,00	7,50	7,53
V		2,72	9,48	7,21	5,68	6,77	7,30
VII		3,18	10,14	7,46	5,92	7,30	7,56
		3,12	10,09	7,58	5,98	7,36	7,72
VIII	Porcelain crucible.	2,62	9,06	6,68	5,30	6,48	6,64
	Porcelain crucible.	2,66	9,40	6,76	5,48	6,36	6,74
	Porcelain crucible. Portions used for 1 hour and recheated for 1 hour.	2,84	8,76	5,50	5,08	6,16	6,54
	Weighing bottle.	3,00	9,70	7,26	6,02	7,24	7,38
	Weighing bottle.	3,18	9,80	7,34	6,00	7,18	7,44
	Weighing bottle. Portions used for 1 hour and recheated for 1 hour.	2,90	9,40	6,92	6,00	6,92	7,07
	Weighing bottle. Portions used for 1 hour and recheated for 1 hour.	3,02	9,38	7,14	9,56	6,92	7,08
X		2,96	9,89	7,47	6,09	7,22	7,37
XI		2,92	9,75	7,26	5,64	7,00	7,25
		2,94	9,85	7,32	5,82	7,18	7,36
XII		2,95	10,27	7,53	6,24	7,30	7,63
XIII		2,83	10,06	7,30	3,90	7,10	7,38
XIV		2,91	9,66	6,87	5,77	6,91	7,01
		2,81	9,45	6,76	5,68	6,67	6,82
		2,74	9,37	6,70	5,61	6,63	6,83
XV		2,94 } 2,96 2,98	9,59 } 9,61 9,62	7,18 } 7,18 7,17	5,49 } 5,52 5,55	7,09 } 7,13 7,17	7,44 } 7 43 7,42
XVI		2,58	9,27	6,78	5,06	6,68	6,67
	MAXIMUM	3,18	10,27	7,62	6,24	7,36	7,72
	MINIMUM	2,54	8,76	5,50	5,08	6,16	6,54
	AVERAGE	2,87	9,64	7,08	5,75	6,98	7,20

TABLE 2.

Results Showing Percentage Lost by Coal when Tested by Methods for Determination of Water Ordinarily Employed by Members of Sub-Committee.

Worker	Particulars of Method				Coal Number					
	Grams of coal	Weighed in	Heated in	Hours	1	2	3	4	5	6
I	1		Gay Lussac water oven at 98°–99°.	½	2,90	9,70	7,10	5,30	7,10	7,20
II	25–30	Brass tray closed when weighing.	Water oven (air oven) at 100°, 105–110°.	Constant weight.	3,15	10,03	7,44	5,91	7,36	7,84
III		Covered copper crucible.	Drying stove with air circulation at 105°.	1½	2,88 2,87 } 2,87	9,33 9,27 } 9,30	6,78 6,59 } 6,68	5,36 5,39 } 5,38	6,91 6,92 } 6,92	7,25 7,23 } 7,24
IV	1	Porcelain crucible.	Toluene bath at 104–107°.	1	3,11	10,06	7,74	6,08	7,56	7,66
V	1	Platinum crucible.	Steam oven under pressure at 105°.	1	2,75	9,63	7,37	5,77	7,09	7,31
VI	4–5	Watch glasses clipped.	Toluene oven.	1	3,15	9,57	7,43	5,32	7,33	7,58
VII	1	Shallow weighing bottle.	Toluene oven at 108°.	1	2,96 2,98 } 2,97	10,16 10,16 } 10,16	7,54 7,64 } 7,59	6,01 5,95 } 5,98	7,63 7,64 } 7,64	7,91 7,98 } 7,95
VIII	1	Weighing bottle.	At 105°.	1	3,06 3,24 } 3,15	9,82 9,92 } 9,37	7,34 7,46 } 7,40	6,04 6,24 } 6,14	7,24 7,32 } 7,28	7,53 7,46 } 7,50
IX	4	Porcelain boat weighed in tube.	Water oven with hot air circulation at 94–95°.	1	2,90	9,69	7,36	5,40	7,06	7,38
X	1	Porcelain crucible.	Air bath at 105°.	1	3,16	10,16	7,79	6,19	7,34	7,45
XI	1	Watch glasses clipped.	V. Meyer toluene oven.	1	2,95	9,86	7,34	5,95	7,28	7,45
XII	1	Watch glasses ground to fit	Water oven.	1	3,12	9,78	7,28	5,46	7,31	7,66
XIII[1]										
XIV	1	Weighing bottle laid on side	Drying stove at 100–110° mean 105°.	½	3,04 3,10 3,00 } 3,05	9,98 10,03 10,09 } 10,03	7,51 7,53 7,52 } 7,52	6,20 6,13 6,24 } 6,19	7,56 7,47 7,51 } 7,51	7,71 7,87 7,77 } 7,78
XV	1	Weighing bottle.	Large toluene oven at 103°	2	2,94 2,98 } 2,96	9,59 9,62 } 9,61	7,19 7,17 } 7,18	5,49 5,55 } 5,52	7,09 7,17 } 7,13	7,44 7,42 } 7,43
XVI	2	Watchglasses taredagainst Similar glasses.	Water-oven.	To constant weight.	2,90	9,48	7,12	5,24	6,95	7,07
Maximum					3,16	10,16	7,79	6,19	7,64	7,95
Minimum					2,75	9,30	6,68	5,27	6,92	7,07
Average of Average Results					2,99	9,76	7,33	5,71	7,23	7,47

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[1] See remarks on the table.

XII.—Used in connection with a contract which specifies that the coal shall be dried at 100°—not used by choice.

XIII.—The method ordinarily employed by this worker is to crush rapidly any lumps in a sample with a wooden mallet on a thick steel plate, and then to weigh 50 grammes in an iron box 300 mm., 200 mm., 50 mm. high. This box is placed on the bottom of a large oven heated by coal for 15 minutes at a temperature of about 110°; it is then lifted to the lower shelf where it remains for 3¼ hours at a temperature of 85–95°. It is then removed and covered, and weighed when it is cold.

The larger samples of coal required for this method were sent in bags, and on examination were found to contain less moisture than the small samples in tins. The following table shows the agreement of this method with the others employed:

	1	2	3	4	5	6
1 hour at 105°	1,10	"	6,20	6,30	6,80	5,00
2 hours at 105°	1,05	"	6,20	6,15	6,60	4,80
24 hours vacuum over H^2SO^4	1,20	"	6,00	5,50	6,20	4,20
Above method	1,20	"	5,90	5,64	6,64	4,93

XIV.—The weighing bottle used is 50–70 mm. high and 27 mm. diameter. It is weighed laying on its side and one gramme or thereabouts of coal introduced; the stopper is then fitted and the total weight taken. The bottle is unstoppered and placed in a stove heated at the start to 110°. The temperature falls to about 102–103° and rises to a temperature of 105°–110°. After 15 minutes the bottle is taken out and put in a desiccator over calcium chloride for 40 minutes. It is then withdrawn and immediately stoppered and weighed. (This method has been described by Pellet and Arnaud.)

The methods ordinarily used by different workers varied very much. The quantity used was in most cases one gramme, but in one case as much as 500 grammes and in others 25–30 grammes and 4–5 grammes were taken. The temperature, or rather perhaps, reputed temperatures varied from 94,5° in the case of a worker at Germiston, Transvaal, which is about four thousand feet above sea level, to that obtained in a toluene bath, which appears to be usually to be considered as from 105° to 107°, although toluene boils at 111°.

It does not appear that any Member of the Committee commonly uses a vacuum method, although some speak highly of this method.

It must be borne in mind that in some cases the adoption of a method does not necessarily indicate that method is specially favored by the Worker as it may be prescribed in connection with a specification not framed by him.

There appears to be a preponderance of practice in favor of some modification of the Standard American Method of drying one gramme at 105° or thereabouts for one hour, but a majority of workers using this method introduce the precaution of using a vessel—either watch glasses, weighing bottle or boat in tube—which can be closed while it is being weighed. We consider that this is a very desirable practice, which should be generally adopted. (Cf. 1 A, pp. 85–89.)

These results are particularly interesting as representing the figure which members would have returned had the samples been sent to them in the ordinary way of practice. For this reason we have averaged the mean results and not all the results obtained as we consider that it would be natural, when there was no reason for preferring one or the other of a set of results to take the mean.

It will be noticed that for every coal the maximum is obtained by the worker using a temperature of 105° or thereabouts, although with the anthracite two workers also who used water ovens were within 0,05 of the maximum. We call special attention to the results marked XIV, obtained by drying for ¼ hour only which are in only one case, more than 0,20 below the maximum, and in one case are as high as any others. The lowest results are those obtained by heating in copper crucibles for one and one-half hours, except for coals N^{os} 1, 4 and 6. It is worth noticing that, although this comparison in no way represents the relative or absolute accuracy of the results, in only one case was the discrepancy greater than 1% and that the greatest variations calculated on the mean *dry matter* were as follows:

1	2	3	4	5	6
0,3%	0,9%	1,2%	0,9%	0,8%	0,9%

These differences are probably in all cases less than the errors incident to sampling from a large bulk.

We do not press the above point of the relative smallness of the discrepancies when considered on the dry matter, as compared with the errors of commercial sampling, for more than it is worth. We fully realize that the occurrence of such large variations between workers, whose methods are relatively free from experimental error, in so far as they each give concordant results, indicates the need of some more definite agreement as to the processes to be used, and further work on the general question of the presence of water in coal and other materials and its determination. Certain aspects of this question are considered in a later section of this report.

1 C

THE VACUUM METHOD

The results obtained by the method of drying in the presence of a desiccant under greatly reduced pressure vary considerably; in fact to such an extent as to militate greatly against the value of the method as one of ordinary application. It is true that, on *a priori* grounds, the method appears to be almost ideal, but apart from the actually observed discrepancies it is clear that many points require attention in order that the results obtained by different workers may be comparable.

If we consider that a substance is air-dry when the vapor tension of the water associated with it is in equilibrium with that of the surrounding air it is clear that a removal of moisture from that air will cause a continual decrease of the amount of water in the substance exposed to it. Such a desiccant as sulphuric acid which even when as weak as 84% has only a vapour pressure (of water) of 0,1 mm. will clearly bring about this decrease until substances which, with it, are exposed to a confined atmosphere are in equilibrium. A reduction, by evacuation, of the partial pressure of other gases or vapors than water will accelerate this process which, except when the initial difference of vapor tension is very high e. g. at high temperatures, will always be very slow. The rate of drying will, if as is most probably the case, the water is absorbed (retained by surface concentration), follow an exponential curve, the slope of which will depend on the rapidity of the exchange through the medium of the vacuous space between the substance to be dried and the desiccant. If the temperature be kept constant this rate will vary with the relative areas of substance and desiccant which are exposed, with the partial pressure of gases other than water vapor, with the absorbtive power, i. e., the vapor pressure of the desiccant, with the volume and form of the vacuous vessel used and the form of the vessel in which the substance to be dried is exposed. In any case the drying relatively rapid at first will soon fall off to a nearly uniform rate which may continue for days and the increments of loss of weight may be so small as to appear negligible whereas their sum over the whole period of drying would perhaps be appreciable. In fact it is difficult to know when to stop.

The results actually obtained by workers bear out this conclusion. In a method such as this which is practically free from manipulative errors it is difficult to explain the great variations obtained by different workers otherwise than by supposing that stagnation of vapor, differences of temperature, small exposure of substance to be dried or of desiccant account for the lowness of some of the results. It may be supposed that in all these cases much longer exposure would have caused a greater loss although there is the chance that even with a fairly good vacuum some compensating gain by oxidation may take place, thus invalidating any results obtained in a badly designed desiccator or with a weak desiccant. When the lowness of the vacuum is a cause of slow drying this possibility of oxidation becomes still greater.

We may consider the series VII conducted in a relatively very high vacuum. The results obtained by drying in 24 hours are in four or say three cases out of six much higher than those obtained in 15 hours. One naturally asks what would the results of 48 or 96 hours' drying be? Possibly the same as those given, but who knows? Where is finality?

TABLE 3.

Results Obtained by Drying in a Vacuum.

Worker	Particulars of Method.				Coal Number					
	Weight taken	Weighed in	Time	Desiccator	1	2	3	4	5	6
I	1 gram.	Porcelain dishes.	36 hours.	H^2SO^4.	2,79	9,60	7,10	5,20	7,00	7,10
II			Constant weight after 3 days.	H^2SO^4. Vacuum 12 mms. Hg.	2,41	9,01	5,93	3,99	5,98	6,87
III	1 gram.	Porcelain dishes.	Constant weight 36 hours.	H^2SO^4 (1,84 sp. gr.)	2,56 2,65 } 2,61	9,89 9,87 } 9,88	7,00 6,94 } 6,97	4,58 4,72 4,52 4,60 } 4,61	6,77 6,86 } 6,82	7,10 7,03 } 7,07
IV	1 gram.		24 hours.	H^2SO^4.	3,11	10,32	7,76	5,81	7,60	7,80
V	2 grams.				2,85	10,17	7,54	5,52	7,51	7,68
VII		Shallow weighing bottle.	15 hours. 24 hours.	Fresh H^2SO^4 (1,84 sp. gr.) Vacuum 1–3 mms.	3,22 3,02 } 3,11 3,63 3,70 } 3,66	10,23 10,22 } 10,12 10,39 10,35 } 10,37	7,78 7,85 } 7,81 7,86 7,80 } 7,83	6,09 6,07 } 6,08 6,10 6,00 } 6,05	7,50 7,56 } 7,53 7,63 7,72 } 7,68	8,01 7,90 } 7,96 8,30 8,41 } 8,36
VIII	1 gram.	Weighing bottle.	24 hours.	Strong H^2SO^4.	2,84	8,80	6,42	3,84	6,41	7,16
IX[1]					2,84 2,92	9,04 9,96	6,62 7,52	3,90 5,42	6,46 7,26	7,04 7,56
X			24 hours. 48 hours.	Strongest H^2SO^4. Desiccator gently moved occasionally.	3,11 3,12	10,25 10,33	7,88 7,98	6,05 6,22	7,74 7,79	8,02 8,08
XI		Clipped watch glasses.	24 hours.	Hempel. Strong H^2SO^4. Vacuum 20 mm. Hg.	3,09	10,31 10,38 10,37	7,74	6,13	7,66	7,82
XII	1 gram.	Boat or weighing tube.	Till constant.	Strong H^2SO^4. Except in 1 (P^2O^5) used. Vacuum 12 mms. Hg.	2,85	10,03	7,52	5,44	7,52	7,76
XIII	1 gram.	Porcelain crucible.	24 hours.	H^2SO^4 66 B. (50 mms. Hg.)	2,60	9 ,60	7,20	4,90	6,80	7,10
XIV	1 gram.	Weighing bottle.	Every 24 hours till constant.	H^2SO^4.	2,95 2,92 } 2,94	10,02 10,00 } 10,01	7,52 7,54 } 7,53	5,75 5,68 } 5,72	7,52 7,51 } 7,51	7,76 7,74 } 7,75
XV	1 gram.	Weighing bottles, 28^{mm} diam., 22^{mm} high.	To constant weight.	P^2O^5.	2,98 2,95	10,26 10,27	7,81 7,79	6,11 6,08	7,66 7,68	7,75 7,71
XVI	1 gram.		To constant weight.	H^2SO^4 below samples preferred.	2,85	9,63	7,20	5,07	7,00	7,11
		Maximum			3,70	10,39	7,98	6,22	7,79	8,41
		Minimum			2,41	9,01	5,93	3,84	5,98	6,87
		Average			2,95	9,97	7,40	5,35	7,27	7,60

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[1] No details.

Professors De Koninck and Huybrechts weighed the samples examined by them at intervals and tabulated the results; for example we give those obtained with N^{os} 2 and 4.

After drying in vacuo over H^2SO^4 for

	HOURS				
	24	48	62	96	120
the loss was:					
N° 2	8,66	9,55	9,76	9,97	10,02
	8,66	9,56	9,74	9,94	10,00
N° 4	5,47	5,57	5,75	5,57	5,44
	5,38	5,52	5,68	5,57	5,49

Here we see that while N° 2 dried continuously at a slowly decreasing rate during five days N° 4, which was of an exceptional character, reached a maximum loss in three days and then began to gain. One may ask again of N° 2—what virtue is there in the maximum period adopted? Judging from the form of the curve and the magnitude of the last loss observed it might be expected that the coal should go on losing a few hundredths of a per cent for some days.[1]

Or what data for the true determination of water do the figures for N° 4 afford? How much lower is the figure 5,68 than the true water content? When did the oxidation, which has undoubtedly occurred, begin to be appreciable? What would be the result of displacing the air in the desiccator with an inert gas before evacuating? Another question which is perhaps not altogether academical arises. Is all the loss moisture or do hydrocarbon and other gases escape from coal under the conditions of experiment?

Experiments by Dr. Pollard with the sample N° 2 showed that when this coal was dried in vacuo at 105° and the loss of weight of the coal determined as well as the gain in weight of sulphuric acid drying tubes, only a very small difference was found, the results being—direct 10,67%, loss 10,58%. This difference it should be noticed was in the direction usually observed, the direct result being the higher pointing to oxidation rather than to excessive loss in a vacuum. Experiments by him with ferrous sulphate showed that this salt was invariably oxidized when dried in an "air vacuum" but not so in a "hydrogen vacuum."

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[1] Cf. Hillebrand, Bulletin, 422 U. S. Geological Survey, p. 68.

A few practical observations may be of interest. The Hempel desiccator appears to be the best form to use since the desiccant can be placed both above and beneath the substance to be dried and thus not only a large but a well distributed drying surface be exposed. To secure fairly rapid drying a moderately high vacuum should be used. We cannot state with certainty that as high a vacuum as within 1 to 3 mm. of barometer is advantageous from all points of view.

The temperature should be fairly constant during the period of drying and not very far from the average temperature—say 15°.

Professors De Koninck and Huybrechts are of opinion that it is advantageous to admit air and re-exhaust every 24 hours rather than to expose for long periods without some circulation. They, and several other workers point to the desirability of drying the air before admitting it into the desiccator. Dr. Pollard gives some figures in support of this:

	COAL			
	N° 1	N° 2	N° 3	N° 4
Vacuum filled with dry air before opening.........	3,09	10,47	7,80	6,28
Air not dried.............	3,02	10,31	7,74	6,13

He further illustrates the absorptive power of coal N° 2 after it is dried, as follows: "Air was sucked over 5 grams of dried coal and then through a sulphuric acid U tube for six hours. The coal gained 0,121 grams and the U tube only 0,008 grams, so the coal had nearly dried the air."

It appears to be important that the vessel in which the coal is weighed should be both shallow in form, exposing a large surface of coal and by reason of its low sides allowing free exchange with the surroundings and closable in such a manner as to exclude moist air during the period of weighing.

We shall return to this point later when dealing with the general question of apparatus.

SECTION 4

Methods of determining water other than those indicated in the President's circular letter of October and included in the preceding sections:

- *a*, Drying in a water oven.
- *b*, Drying in a current of inert gas.
  - (−) Indirect determinations—loss of weight of coal.
  - (+) Direct determinations—gain of weight of drying tube.
- *c*, Drying for ¼ hour at 105° of varying weights of coal spread over varying surfaces.
- *d*, Drying at 105° for varying times (¼ hour to 2 hours).
- *e*, Drying in desiccators at ordinary pressure.
- *f*, Expulsion of water by boiling coal with xylene and measuring the volume of water evolved.

4*a*.—Several workers have made series of experiments in which coal is dried in the water oven. The results are given in table 4*a*. It will be noticed that the figures on the whole agree more closely than those obtained by drying at a higher temperature or in a vacuum. They are, however, in all cases, but the maxima obtained on 1 and 3, lower than the average results obtained by drying at 104–107° or by drying in a vacuum. It seems clear that either (1) the temperature reached in a water oven is insufficient to drive off all the moisture, except perhaps in a carefully dried atmosphere, or more probably (2) owing to the slow rate of drying the gain of weight due to oxidation seriously diminishes the loss of water.

An exploration by the Vice-President of a large water oven 22,5 cm., 25,5 cm., 32,5 cm., by means of a thermo couple showed that the temperature varied considerably in different parts, temperatures as low as 16° below that of steam having been recorded. The effect of opening the large door (22,5 cm., 25,5 cm.) was very marked, since the thermo couple, which has no appreciable lag, did not attain a stationary temperature for some minutes after each opening. It was noticed that, although the door was by no means air tight, the closing of the little damper in the

TABLE 4A

RESULTS SHOWING PERCENTAGE LOST BY COAL WHEN DRIED IN WATER OVEN FOR PERIODS STATED.

Worker	Grams of coal	Time of Heating Hours	Coal Number 1	2	3	4	5	6
I	1	½	2,90	9,70	7,10	5,30	7,10	7,20
		1	2,70	9,60	6,80	5,30	6,90	7,10
		1½	2,80	9,70	7,10	5,30	6,80	7,10
		2	2,70	9,70	7,10	5,30	6,80	7,30
VIII	1 (W.B.)	1	3,12	9,76	7,30	5,50	7,00	7,48
IX[1]	4	½	2,90	9,69	7,36	5,40	7,06	7,38
XII	1	1	3,12	9,78	7,28	5,46	7,31	7,66
XVI	5	(In dishes till constant weight.)	2,86	9,42	7,08	5,25	6,72	6,95
	2	(Watch glasses until constant.)	2,90	9,48	7,12	5,27	6,95	7,07
		MAXIMUM	3,12	9,78	7,36	5,50	7,31	7,66
		MINIMUM	2,70	9,42	6,80	5,25	6,72	6,95
		AVERAGE	2,89	9,65	7,14	5,34	6,96	7,25

[1] See 2.

door raised the temperature about 0,7° even on the bottom of the bath at the back.

Experiments by Messrs. Andrews, Coste and Powney on a very moist coal examined by them (see p. 85) seem to show that at a temperature below 100° the loss of water is so much less rapid than at 105° that a true figure for moisture cannot be obtained within a reasonable time, although the heating be continued some hours in an inert atmosphere.

The uncertainty as to the temperature in a large water oven, although, judging from the small differences between the loss in one hour at 79° and a reputed temperature of 100°, viz., 0.21%, its effect is not great, renders the use of this appliance undesirable for exact moisture determinations and we cannot recommend it. *We feel that the mere fact that the range of temperature between, say* 80° *and* 98°, *appears to be a particularly insensitive one, and therefore allows very concordant results to be obtained under varying conditions, induces a false sense of security which a few experiments at* 105° *will completely shatter.*

4b.—The method of drying at 104–107° in a current of gas free from oxygen appears to possess a considerable advantage over any other process of drying at an elevated temperature in that the necessary compromise between the desire to dry completely on the one hand and the fear of oxidation on the other is reduced to a minimum. It may be said, at any rate when "fixed" gases such as hydrogen, nitrogen or carbondioxide are used, that the only reasonable possibility of error is the loss of something other than water due to the elevated temperature adopted. That this is small, at least for some coals, has been shown by Mahler (*Comptes rendus*, 1910, 1521, 2). The use of coal gas unless carefully purified would seem to be very risky as is shown by the results marked VIII. It is, perhaps, not unreasonable to suppose that dry coal may possess a certain power of ad- or ab-sorbing some of the constituents of coal gas. This possibility is suggested by Dr. Lessing whose figures seem to confirm this view; Mr. Hills, who uses a direct method, i. e., actually weighs the water in calcium chloride tubes, informs us that, since the amount of CO^2 in coal gas has become considerable, owing to the abandonment of purification

TABLE 4B.

Showing Percentage (−) Lost by Coal and (+) Water Gained by Drying Tube when Coal is Dried in a Current of "Inert" Gas at a Temperature of 100–110°.

Worker	Coal weighed in	Dried in current of	Coal Number											
			1		2		3		4		5		6	
			−	+	−	+	−	+	−	+	−	+	−	+
II	Porcelain boat.	CO^2. H^2.	2,93 2,84 2,96 2,88		10,12 9,78 9,84 9,46		7,46 7,30 7,10 7,50		5,88 5,89 5,58 5,62		7,31 7,10 6,65 6,90		7,95 7,67 7,50 7,54	
IV	U tube at 100°.	Coal gas (purified)		3,15 ($Ca Cl^2$)		10,46 ($Ca Cl^2$)								
V	Boat at 110°.	N^2.	2,65		10,18		7,73		6,24		7,38		7,61	
VIII[1]	Special drying tube.	Coal gas (dried).	2,52		7,87		6,66		6,26		5,98		6,40	
XII	Nickel boat exploding.	CO^2.	2,87	2,85 $H^2 SO^4$	10,44	10,20 $H^2 So^4$	8,03	7,83 $H^2 So^4$	6,51	6,62 $H^2 So^4$	7,85	7,87 $H^2 SO^4$	8,12	7,89 $H^2 So^4$
XV	Platinum or porcelain boat.	N^2.	2,72 2,87	2,62 3,03 $Ca Cl_2$	10,61 10,54	10,54 10,62 $Ca Cl^2$	7,66 7,77	7,91 8,18 $Ca Cl^2$	6,33 6,27	6,41 6,36 $Ca Cl^2$	7,59 7,54	7,98 7,90 $Ca Cl^2$	7,53 7,62	7,94 7,72 ($Ca Cl^2$)
	Maximum		2,96	3,15	10,61	10,62	8,03	8,18	6,51	6,62	7,85	7,98	8,12	7,94
	Minimum		2,52	2,62	9,46	10,20	7,10	7,83	5,58	6,36	6,65	7,87	7,50	7,72
	Average		2,84	2,91	10,12	10,40	7,57	7,97	6,04	6,46	7,29	7,92	7,69	7,85

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[1] Not included in average for reason stated in text.

with lime, he has found it necessary to take special precautions for the removal of this gas (CO^2), since calcium chloride usually contains sufficient free lime for it to absorb CO^2 readily. His two results by this positive method and those of Drs. Constam and Pollard are particularly interesting, as they show that at least the amount of water indicated is actually given off from the coal, since calcium chloride, unlike sulphuric acid, is not an absorbent of olefines. It is worthy of note that in four coals out of the six sent out the highest result obtained by any method was by this method.

Two series in which the coals were dried at 105° in a current of dry air and the loss of weight compared with the gain of a drying tube were intended to show the differences between the direct and indirect methods when the influence of oxygen is not excluded.

Worker	Coal Number											
	1		2		3		4		5		6	
	−	+	−	+	−	+	−	+	−	+	−	+
XI	3,15	3,25	10,31	10,68	7,78	8,18	6,09	6,34	7,54	8,01	7,84	8,28
XII	3,19	3,23	10,22	10,38	7,52	8,29	6,42	6,56	7,47	8,37	7,92	8,25

The reporters feel that these results, especially those in which one of them was concerned, and in fact all comparisons of the direct and indirect methods, would be more convincing if accompanied by a statement that a drying tube, placed between the apparatus used to dry the gas and the coal which is being dried, and exactly similar to that in which the evolved water is collected, neither gained or lost in weight during the experiment. Without this information it is futile to theorize as to the difference between the results of the two methods as they may be altogether independent of the coal itself. It is, however, only fair to state that Dr. Pollard found with coal N° 2 that the difference between loss and gain in a current of hydrogen at 105° was only 0,07%

Dr. Constam, who ascribes the differences between his results by this method and by the vacuum method to the fact that three weeks elapsed between the two sets of determinations, says: "Diese Methode ist eine äusserst subtile und schwer zu handhabende." We endorse this statement in so far as it refers to the direct method, but see little difficulty in an accurate determination of loss in a current of inert gas.

4*c*.—Professors De Koninck and Huybrechts have experimented with very varying weights of coal dried in weighing bottles of differing areas of cross sections for ¼ hour at 105°. Their results are as follows:

	1		2		3		4		5		6	
1 gram[1] 0,19 grams per sq. cm.	3,04 3,10 3,00	3,05	9,98 10,03 10,09	10,03	7,51 7,53 7,52	7,52	6,20 6,13 6,24	6,19	7,56 7,47 7,51	7,51	7,71 7,87 7,77	7,78
1.5 grams[1] 0,28 grams per sq. cm.	3,00 3,01	3,01	10,16 10,13	10,14	7,69 7,58	7,63	6,00 5,84	5,97	7,53 7,60	7,56	7,83 7,83	7,83
5 grams[2] 0,16 grams per sq. cm.	2,98		9,94		7,53		6,08		7,53		7,77	
7,5 grams[2] 0,25 grams per sq. cm.	3,00		10,02		7,76		6,15		7,60		7,85	
10 grams[2] 0,33 grams per sq. cm.	2,95		9,65		7,27		Not determined.					

This very interesting series points the moral that it is not so much the amount of coal taken for an experiment as its surface of exposure that matters in determining the amount of moisture in a sample. The significance of the results obtained may be summarized in the statement that:

At a temperature of 105° (provided the air current is sufficient) no appreciable difference in results of moisture determinations need be anticipated, provided the coal is distributed evenly over the bottom of the containing vessel and a concentration of not more than 0,3 grams per square centimeter of exposed surface is allowed.

The worker suggests that one gram would in practice be too small a weight for the reason that the samples are not generally prepared with the same care as those submitted in the present research. This is undoubtedly the case and it might be found convenient by those who have two samples of each coal prepared (i. e., a quickly ground sample for moisture and a finely ground sample for analysis and determination of calorific power) to determine the moisture in the coarse sample on five grams and in the fine sample on one gram.

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[1] Weighing bottle 50 to 70 mm. high and 27 mm. diameter = 5,7 } sq. cm. cross section.
[2] —— —— 30 mm. high and 60–63 mm. diameter =30,4 }

It is worthy of especial note that, in the above experiments, the healing was continued for ¼ hour only.

4d.—The same workers as investigated the effect of varying the amount of coal taken, also studied the effect of time of drying on the results.

Their figures are given in the table below:

One gram of coal dried at 105°.

	1	2	3	4	5	6
a) For 15 min. (mean see table 2, XIV)..	3,05	10,03	7,52	6,19	7,51	7,78
b) For another 20 min..	3,04 3,04 3,00 } 3,03	9,92 9,95 10,04 } 9,97	7,33 7,34 7,34 } 7,34	6,16 6,09 6,26 } 6,17	7,46 7,41 7,44 } 7,64	7,63 7,65 7 64 } 7,64
c) For 1 hour (mean see table 1, XIV)..	2,79	9,77	7,13	6,00	6,99	7.13
d) For 2 hours (mean see table 1A, XIV).	2,82	9 ,49	6,78	5,69	6,74	6,89

TABLE 4C.

	Coal Number					
	1	2	3	4	5	6
1 gram[1]. 0,19 grams per square cm.	3,04 3,10 3,00 } 3,05	9,98 10,03 10,09 } 10.03	7,51 7,53 7,52 } 7,52	6,20 6,13 6,24 } 6,19	7,56 7,47 7,51 } 7,51	7,71 7,87 7,77 } 7,78
1.5 rams[1]. 0,28 grams per square cm.	3,00 3,01 } 3.01	10,16 10,13 } 10,14	7,69 7,58 } 7,63	6,00 5,94 } 5,97	7,53 7,60 } 7,56	7,83 7,83 } 7,83
5 grams[2]. 0,16 grams per square cm.	2,98	9,94	7,53	6,08	7,53	7,77
7,5 grams[2]. 0.25 grams per square cm.	3,00	10,02	7,76	6,15	7,60	7,85
AVERAGE.........	3,01	10,03	7,61	6,10	7,55	7,81

From these results it would appear that the short period of ¼ hour possesses some advantages over any longer period, in so far as the loss of water appears to be as great and the gain by oxidation of the coal certainly seems to be much less. The period of two hours certainly seems to be long.

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[1] Weighing bottle 50 to 70 mm. high, and 27 mm. diameter; Cross sectional area=5,7 square cms.
[2] Weighing bottle 30 mm. high, and 60–63 mm. diameter; Cross sectional area=30,4 square cms.

4 *e.*—One group of workers (XII) dried the coals, in watch glasses, in an ordinary desiccator, the results obtained being:

1	2	3	4	5	6
2,96	9,95[1]	7,18	5,20	7,28	7,53

The method, which required several days for a relatively constant weight to be reached, is obviously too slow for technical purposes, but taking the higher results obtained by any worker as representing the correct values, it will be seen that the following supposed percentages of the total water were lost by mere exposure to dry air.

1	2	3	4	5	6
78%	95%	90%	80%	93%	90%

These workers found that the coal experimented with by them, which contained 13,90% of water (lost at 105°), could, when dried, be rehydrated up to within 1,5% of its original weight by exposure to a moist atmosphere.

Dr. Dudley, a member of the American Committee, considered that for coals containing about 2% of moisture satisfactory results could be obtained by drying in a watch glass for 24 hours at atmospheric pressure and temperature over sulphuric acid. The method is not recommended by him for lignites and coals with high moisture.

We do not consider that the method possesses any advantages over other methods which excel it in both accuracy and celerity.

f.—Xylene Method.

Dr. Constam gives some results obtained by his colleague Dr. Schläpper with a modification, not hitherto published, of a method described by Marcusson for the estimation of water in oils, fats, soaps and resins.

40–50 grams of coal (100 grams of coal of low water content) are weighed into an Erlenmeyer flask of 500 cc. capacity, 200 cc. of xylene are added and 150 cc. of this are distilled over, the flask being heated on a sand bath, into a measuring cylinder, the lower part of which is divided to 1/20 cc. The measuring vessel is then hung in a cylinder with warm water. Any drops of water which hang about the shoulder of the measuring vessel are detached and allowed to fall to the narrow part by means of a glass rod. After 1 hour standing, the volume of the water distilled over with the Xylene and which has separated under it, is measured, due correction being made for the meniscus.

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[1] A series of tests with this coal was carried out by Dr. Pollard, using various desiccants. The results will be given in the section on appliances.

The results obtained are given below:

Coal N°	1	2	3	4	5	6
	3,00	10,38	7,80	6,16	7,74	7,60

The method is ingenious and in the opinion of the reporters has many advantages and might be well made the subject of further trial by other workers.

SECTION 5

(I) The actual percentage of water in the samples, and

(II) The treatment of samples of coal when received.

The question as to the actual percentage of water in the samples sent out by the President and received by the workers is of importance. The method of preparation of these samples is fully described on page 6 of this report. It appears to have been approved generally by the recipients, only one of whom remarked on the circumstance that the rubber solution did not appear to have made a tight seal. Even so the exchange of air or water between the tins and their lids must have been very small.

It was, however, considered desirable to determine the water in the sealed tubes which were taken during the filling of the sample tins. Mr. G.-N. Huntly and Mr. E.-R. Andrews, to whom our best thanks are due, kindly undertook this work. The former gentleman, whose results are marked H, dried for one hour in a toluene bath at 108° in glass weighing bottles, cooling in a desiccator with fresh sulphuric acid. Each figure is the mean of two agreeing determinations. Mr. Andrews dried in a nickel boat placed in the tube air bath described by the Vice-President (*Journ. Soc. Chem. Ind.*, 1896, 421) through which a current of dry, oxygen-free CO^2 was passed. These results are marked A. The time sequence of the pealing of the samples in the tubes was not noted, but we have arranged in an ascending order in the following table, in which we also show the highest and the lowest of the maximum results obtained by individual workers.

We discuss these results with a view to obtaining a working convention as to the probable moisture content of the coal in the tins sent out and in no way wish to criticise the work of the many colleagues who have assisted in the deliberations of the Committee.

TABLE 5A.

Coal N°.	1	2	3	4	5	6
Lowest maximum obtained by any worker.........	2,85 2,75 (A) 2,81 " 2,84 " 2,85 " 2,86 " 2,90 (H)	9,59 9,81 (H) 9,87 " 9,88 " 10,03 (A) 10,15 " 10,20 " 10,40 " 10,49 "	7,00 7,04 (A) 7,28 " 7,46 (H) 7,48 (A) 7,49 (H) 7,69 (A) 7,91 "	5,27 5,71 (A) 5,77 5,77 5,90 6,00 (H) 6,01 " 6,01 " 6,26 (A)	7,00 6,89 (A) 7,15 " 7,26 (H) 7,28 " 7,35 " 7,35 (A) 7,54 " 7,64 "	7,11 6,68 (H) 7,30 " 7,60 (A) 7,61 (H) 7,86 (A) 7,86 " 7,89 " 7,91 "
Greatest difference between tubes.................	0,15	0,68	0,87	0,55	0,75	1,23
Highest maximum obtained by any worker.........	3,70	10,61	8,04	6 51	7,98	8,41
N°. of workers obtaining higher maximum than found in tubes.	13	1	4	2	6	4

It will be noticed that, in no case is the highest percentage of water found in the tubes so high as the highest found by individual workers in the tinned samples and that in samples 1 (3 tubes), 5 (1 tube), 6 (1 tube) some of the tubes contained less water than was found in those tins which yielded the lowest maxima. We cannot help feeling that the tubes are not, on the whole, as reliable as the tins. It is probable that the operation of sealing, however carefully conducted, caused some loss of water by convection currents. It is certainly remarkable that in the case of each sample, some tins gave higher results than the tubes.

We consider the probable water content of the tins of coal to be well within the limits given below:

N° 1, 2,8% to 3,2%.

The maximum result, 3,7 appears to be abnormal and we cannot feel that it represented the true water content of the sample examined.

N° 2, 10,1∓0,5% 9,6% to 10,6%.

This coal was very hydroscopic and it is possible that its water content may have altered during sampling. The series of tube figures shows a progressive increase.

N° 3,	7,0% to 8,0%.
N° 4,	5,3% to 6,5%.

This coal presented special difficulties owing to its high sulphur content.

N° 5,	7,0% to 8,0%.
N° 6,	7,1% to 8,4%.

We have considered the maximum results of individual workers because it appears to us that the probability of obtaining too high results is by all the methods described extremely small, while methods of drying in air baths, water baths and all baths without proper circulation of hot air, and the vacuum methods are likely to give low results, even with ordinary careful work.

The table 5*b* of maximum results obtained on each coal by individual workers is interesting although as we have by our above mentioned estimates of the probable amounts of the water contents of the samples indicated, it is hard to conclude whether it should be taken as illustrating the difficulties of the sampler of those of the analyst.

TABLE 5B.

SHOWING THE MAXIMUM FIGURES OBTAINED BY EACH WORKER ON EACH COAL AND THE METHODS USED.

Worker		1	2	3	4	5	6
I	Method.	(2)	(2)	(2,3)	(2)	(2)	(2)
	Result.	2,90	9,70	7,10	5,30	7,10	7,20
II	Method.	(2)	(1a)	(1a)	(1a)	(1a)	(1a)
	Result.	3,15	10,25	8,00	6,05	7,68	8,16
III	Method.	(1a)	(3)	(3)	(1b)	(1b, a)	(1a)
	Result.	2,92	9,89	7,00	5,91	7,21	7,48
IV	Method.	(4bdi)	(4bdi)	(3)	(1a)	(3)	(3)
	Result.	3,15	10,46	7,76	6,08	7,60	7,80
V	Method.	(3)	(4bi)	(4bi)	(4bi)	(3)	(3)
	Result.	2,85	10,18	7,73	6,24	7,51	7,68
VI	Method.	(2=1a)	(1a)	(1a)	(1a)	(1a)	(2=1a)
	Result.	3,15	9,59	7,47	5,38	7,38	7,58
VII	Method.	(3)	(3)	(3)	(3)	(3)	(3)
	Result.	M 3,70	10,39	7,86	6,10	7,72	M 8,41
VIII	Method.	(1a)	(1a)	(1a)	(4bi)	(1a)	(1a)
	Result.	3,24	9,92	7,46	6,26	7,32	7,53
IX	Method.	(3)	(3)	(3)	(3)	(3)	(3)
	Result.	2,92	9,96	7,52	5,42	7,26	7,56

Worker		1	2	3	4	5	6
X	Method.	(1a)	(3)	(3)	(3)	(3)	(3)
	Result.	3,16	10,33	7,98	6,22	7,79	8,08
XI	Method.	(3)	(3)	(3)	(3)	(3)	(3)
	Result.	3,09	10,31	7,74	6,13	7,66	7,82
XII	Method.	(1a)	(4bi)	(4bi)	(4bdi)	(4bdi)	(4bi)
	Result.	3,19	10,44	8,03	M 6,62	7,87	8,12
XIII	Method.	(1a)	(1a)	(1ab)	(1b)	(1a)	(1b)
	Result.	2,96	10,16	7,30	5,90	7,20	7,38
XIV	Method.	(2=4c)	(4d)	(4d)	(4)	(4)	(2=4c)
	Result.	3,10	10,16	7,76	6,26	7,60	7,87
XV	Method.	(4bi)	(bi)	(4bdi)	(4bdi)	(4bdi)	(bdi)
	Result.	3,03	M 10,61	M 8,18	6,41	M 7,98	7,94
XVI	Method.	(2)	(3)	(3)	(2)	(3)	(3)
	Result.	2,90	9,63	7,20	5,27	7,00	7,11
	AVERAGE.	3,09	10,12	7,63	5,97	7,49	7,73

II.—An important point to consider in connection with the discrepancies observed between the results of different workers is the effect of exposure to the atmosphere on the moisture content of coals. The results of examination of the sealed samples made by Messrs. Andrews and Huntly point to the probability, even when the greatest care is exercised, and the coal is allowed some days to attain a state of equilibrium with the atmosphere, variations in the water content may occur in the sort period necessary for putting up several sets of samples. These differences were probably greater than would occur in ordinary practice, owing to the fact that the coals were very finely ground.

The following series of determinations by Mr. McArthur Johnston (IX) are as he states "Interesting and perhaps instructive as showing the liability of difficulty in obtaining exact agreement on such class of material at different altitudes and atmospheric conditions."

	First Series		2 or 3 weeks after	
	Vacuum.	Laboratory Method.	Vacuum.	Laboratory Method.
Nº 1	2,92	2,90	2,78	2,65
Nº 2	9,96	9,69	9,61	9,47
Nº 3	7,52	7,36	7,04	6,99
Nº 4	5,42	5,40	5,28	5,15
Nº 5	7,26	7,06	6,99	6,75
Nº 6	7,56	7,38	7,09	6,98

Mr. Johnston, who works at Germiston, Transvaal, about four thousand feet above sea-level says of these results: "I ascribe these low figures in the second set to the fact that on opening the tins for weighing purposes a certain amount of moisture was lost by the samples on account of the lower barometric pressure here and of the dry atmosphere as compared with your climate when the samples were crushed and sampled."

Mr. Edgar Stansfield (Canada) prepared a series of small tared tubes and weighing bottles which were quickly filled as each tin was opened and mixed. About ten to fifteen minutes was taken in dealing with each tin. The tubes were reweighed and were used as required for determinations, each tube being again weighed before emptying of its contents for use in an experiment. Notwithstanding the care taken and the fact that the tubes were all stored in the same glass container some lost and some gained when they were reweighed. An epitome of the variations is given below:

Coal N° 1.	+0,0003 gm. to −0,0008 gm.
Coal N° 2.	+0,0012 gm. to −0,0076 gm.
Coal N° 3.	+0,0004 gm. to −0,0028 gm.
Coal N° 4.	+0,0013 gm. to −0,0008 gm.
Coal N° 5.	+0,0015 gm. to −0,0069 gm.
Coal N° 6.	+0,0002 gm. to −0,0020 gm.

The tubes were kept for periods of from one to thirteen days and contained on the average 1,30 grams each. They were closed with corks impregnated with paraffin wax. Mr. Stansfield discusses the relative possibilities of oxidation from inleak of air and from loss of moisture. We understand from him that he proposes to incorporate his work in the Report of the Department of Mines, Canada, which will be printed probably before this report appears. The work, which is highly interesting, will therefore be available in that form. It would obviously be hardly desirable to include the results of the examination of samples which had been subjected to such vicissitudes of climatic conditions in the ordinary tables and it would be difficult to do justice in his work except by giving a very full abstract with several tables.

We think that the safest plan in dealing with finely ground samples of coal under conditions of humidity differing widely from those prevailing at the time of sampling would be (1) to weigh a large quantity into a shallow dish or better a metal tray and to allow say 24 hours for it to reach a state of equilibrium with the atmosphere, longer may be necessary, and then to weigh again and to use this sample. The weight relation of which to the original is known for the determination of water, etc. It should be kept in a tightly stoppered bottle. Or (2) a series of closely stoppered weighing bottles, already weighed and preferably very small might have a measured quantity of coal known to weigh approximately one gram shot into each, from a little scoop or spoon of suitable size. They could then all be weighed and afterwards put in a large air-tight vessel—say a desiccator vessel—which is filled with CO^2. When a determination is to be made a little can be taken out and the whole of its contents, as far as may be, tipped into the weighed vessel to be used for drying or other determination and the bottle reweighed. By this means a weight slightly less than that originally in the bottle is taken and the error of assuming that the weight—probably a few milligrams—left behind represents the coal in its original state is inappreciable. So that however long a period after the bottling-off may elapse before a small sample is used any change in weight such as is noticed by Mr. Stansfield is negligible, so long as it is not so great as obviously to affect the whole character of the coal. An example will make this clear.

b)	Weight of bottle and coal at time of filling	13,5061	gram.
a)	" bottle	12,4321	–
	Coal in original state	1,0740	–
c)	Weight of bottle+coal after say 3 weeks	13,5032	–
	Alteration	0,0029	–
c)	Is taken for information only.		
d)	Weight of watch glasses to be used for drying	11,6317	—
b)	As above	–13,5061	
e)	Weight of bottle from which coal has been tipped out	–12,4379	
	Weight of coal taken for moisture determination	1,0682	–

	Weight to be taken as total weight before drying	13,6999 gram.
f)	Weight after 1 hour drying	13,5637 —
	Loss (= water)	0,1312 gram.

The proportion of total alteration 0,0029 is inappreciable on the 0,0058 gram. left in the bottle and therefore a (virtual) correct weight of original coal can be obtained by this means.

Another plan which we think on the whole will probably be found, when sufficient work has been done, to be most convenient in all cases for the determination of water in a bulk is to weigh 50 or 100 grams and to determine the water by the xylene method mentioned by Dr. Constam.

We do not advise that ground samples of coal should be emptied from the containing vessel and spread out for mixture unless a portion is set apart each time to form a determination of water before mixing the sample. It is safer to place the sample in a cool place for some time and then to stir it with a spatula before taking out a portion for a determination of water.

Section 6

APPLIANCES

Weighing Vessels

We have referred to the advantage of vessels which can be properly closed for weighing coal. Some definite figures in illustration of this can be adduced from the work on the subject by Dr. Pollard.

Samples of coals N^{os} 2 and 3, after being dried and weighed, were left uncovered on the balance and reweighed. N° 2 gained 0,28% in ten minutes, 0,44% in twenty minutes. Air in balance case 68% saturated.

N° 3 gained 0,59% in twenty minutes. Air in balance case 77% saturated.

The need for covering coal while it is being weighed is apparent.

The effects of using different vessels and, incidentally, the greater hygroscopicity of partly oxidized coal (2 hours drying) are shown below. Samples of N° 2 coal which had been dried were left in the balance case, the crucibles open, but watch glasses clipped:

Dried by method	Crucibles		Watch glasses	
	1a	1b	2a	2b
Gain in ½ hour	1,82	2,38	0,26	0,15
	1,83	2,36	0,26	0,19
Gain in 18 hours	5,86	6,41	1,74	0,55
	5,78	6,38	1,74	1,95

a. 1 hour. *b*. 2 hours. Saturation of air 58–63%.

It will be noticed that one pair of watch glasses fitted better than the others. Mr. Andrews has also noticed this.

It is clear, therefore, that well covered vessels are best. Their form is of some importance. Two experiments by Mr. Andrews illustrates this point which has already been referred to as offering a probable explanation of some discrepancies between results.

Portions of about one gram of coal N° 2 were weighed respectively:

a) in (1) a tall weighing bottle 43 mm. high × 27 mm. diameter,
(2) a shallow weighing bottle 25 mm. high × 50 mm. diameter and
(3) a pair of watch glasses 50 mm. diameter.

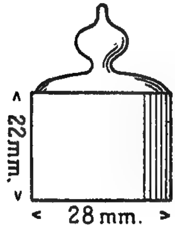
These were all placed uncovered in a Hempel desiccator over and under sulphuric acid and the pressure reduced by a water pump to 30 mm.

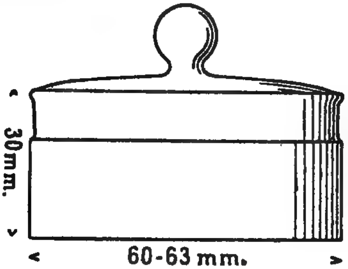
b) In a second experiment two tall weighing bottles one (1) in an upright position, the other (1a) on its side and the shallow bottle were placed in the desiccator. In this experiment the coal in the shallow bottle was carefully distributed over the whole of the bottom. The vacuum in this case was about 18 mm.

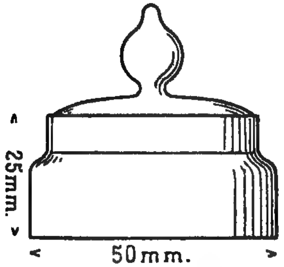
	(*a*) 30 mm.	(*b*) 18 mm.
Loss after..........	22 hours.	18 hours.
(1)	9,44	10,21
(1 *a*)		10,26
(2)	10,03	10,38
(3)	10,22	

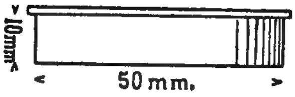
There is good evidence that shallow wide vessels are to be preferred, and some reason for thinking that a high vacuum has a considerable effect in equalizing differences due to varying distribution of the coal to be dried.

Various patterns of weighing bottles have been described and used by Members of the Sub-Committee. Four of these are illustrated by the accompanying sketches.









Dr. Constam and Mr. Huntly use a bottle with straight sides, 28 mm. diameter and 22 mm. high.

Professors De Koninck and Huybrechts use one 60 to 63 mm. diameter and 30 mm. high.

The Vice-President and his colleagues have used one 50 mm. diameter and 25 mm. high with a shoulder. They consider, however, that the most suitable vessel would be one like the lower half of a small Petri cultivating dish with a ground flat plate which would either lie on the ground edge of the dish or be pressed to it by a clip. Such a vessel would have the low sides of a watch glass with the flat bottom of a weighing bottle.

Well fitting watch glasses are very simple and are apparently quite satisfactory.

Desiccators

We find that sulphuric acid, phosphoric anhydride and calcium chloride all appear to be used by workers, although there appears to be some feeling against the use of the latter material. Dr. Pollard has made experiments on the behaviour of these desiccants, some of which we may usefully quote.

He exposed coal N° 2 at ordinary temperature and pressure in desiccators with the drying agents in each case placed both above and below the coal. His results are shown below:

Drying Agent	Per cent Loss			
	After 3 days		After 1 week	
Sulphuric acid	9,89	9,72	10,04	9,88
Phosphoric anhydride	10,06	10,08	10,17	10,15
Calcium chloride	9,71	9,69	9,80	9,73

The phosphoric acid desiccator was then pumped out and the coal weighed next day. The percentage loss had gone up to 10,26 and 10,29.

Similar experiments in vacuo (25 mm.) gave:

Drying Agent	Per cent loss			
	After 3 days		After 1 week	
Sulphuric acid	10,49	10,38	10,49	10,39
Calcium chloride	9,82	9,82	9,89	9,89
	After 42 hours			
Phosphoric anhydride	10,44	10,37		

The inferiority of calcium chloride, to both sulphuric acid and phosphoric anhydride is evident. We particularly warn workers against calcium chloride which has not been examined before use, as we have found some which, although sold in a granulated form, presumably as a desiccant, contained 6% of water in which it easily dissolved when gently heated.

The advantages of phosphoric anhydride for ordinary work are apparent rather than real. It requires careful stirring whenever it is exposed to the air, and Dr. Pollard informs us that his results were obtained in this way. It is unsuitable for use in an ordinary laboratory. The Vice-President and his collaborators commenced to use it for the vacuum method, but abandoned it as inconvenient, owing to the formation on its surface of glacial phosphoric acid when it used to absorb more than traces of water.

Sulphuric acid is cheap, is easily obtained in a state of high concentration and even when relatively dilute has a very low tension of aqueous vapor. Judging from the experiments above quoted, calcium chloride is either a very slow absorbent of moisture or rapidly attains an appreciable vapor tension.

Some workers, but not all, prefer the Hempel desiccator in which the desiccant is above the substance to be dried. It is easy in this desiccator to have it both above and below and thus to obtain the advantages of both positions. The ordinary Scheibler desiccator as usually used has the disadvantage of exposing a very small surface of sulphuric acid to a relatively large volume of air. We see no reason why the drying shelf should not be raised and enough acid put in the desiccator to reach above the level of the shoulder.

There is no doubt in our minds that Hempel's desiccator with sulphuric acid above and below is the best for either ordinary cooling in a dry atmosphere or for drying in a vacuum, and we recommend its use, more particularly for the vacuum method. We are, further, convinced that it is most desirable that when air is reintroduced into a vacuum desiccator, it should be passed slowly through or over sulphuric acid in order that a rapid inrush of moisture may not occur.

Experiments show that coal will, when dry, absorb appreciable amounts of water from air even in the presence of strong sulphuric acid. We may, perhaps, be forgiven for laying stress on the need for a slow introduction of air. It is advisable, at the beginning, that air should be introduced through a drawn-out capillary, using a screw clip or the thumb and forefinger as a check to the first rush, which soon becomes manageable.

SECTION 7

Summary of Work of the Sub-Committee with Conclusions and Recommendations

It is not easy to assess, on any very philosophical basis, the merits of the various methods used, but the following considerations have guided us in arriving at conclusions and formulating recommendations.

I.—There is evidence that no appreciable amounts of hydrocarbons are lost by coal when it is exposed to temperatures not above, say, 140° for a time much longer than that required for drying it, although there is evidence that traces, which can be detected by suitable means, of gases are lost under certain circumstances and Dr. Prager has evidence of this and is working on the subject. Others have noticed that samples of coal which had been sealed appeared to be under some increased pressure when opened.

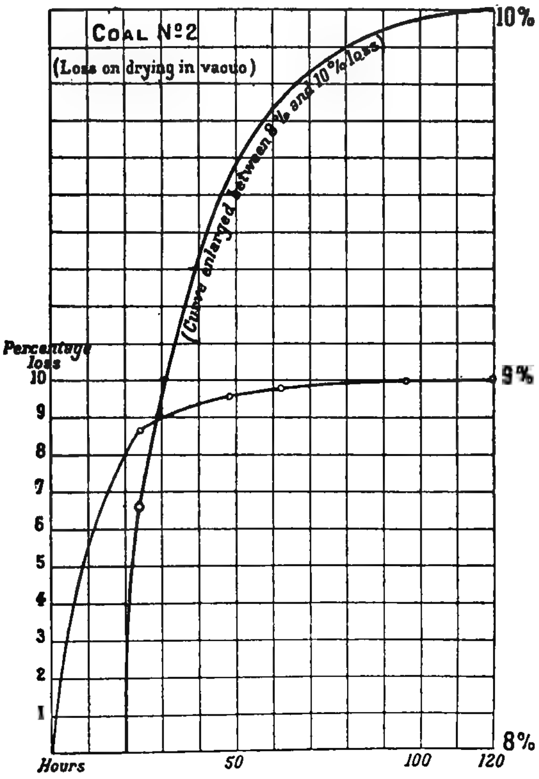
TABLE 7.

AVERAGE PERCENTAGES OF WATER FOUND BY DIFFERENT METHODS.

Method	1	2	3	4	5	6
1 a	2,96	9,84	7,33	5,84	7,20	7,48
1 b	2,87	9,64	7,08	5,75	6,98	7,20
2	2,99	9,76	7,33	5,71	7,23	7,47
3	2,95	9,97	7,40	5,35	7,27	7,60
4 a	2,89	9,65	7,14	5,34	6,96	7,25
4 b Loss.	2,84	10,12	7,57	6,04	7,39	7,69
4 b Gain.	2,91	M(1) 10,40	M 7,97	M 6,46	M 7,92	M 7,85
4 c	M 3,01	10,03	7,61	6,10	7,55	7,81
4 f	3,00	10,38	7,80	6,16	7,74	7,60

(1)M = Highest of the average figures for each coal.

II.—Since the loss of weight when coal is heated to the temperature mentioned above is not appreciably affected by the evolution of hydrocarbons from the coal, the only serious source



of error in properly conducted experiments at that temperature is oxidation of coal, which causes an increase of weight as drying is prolonged. The highest results may therefore be taken as the most correct. A consideration of the tables 5*b* and 7 will show at a glance which methods have been found to give the highest results with the various coals.

The question of the detection of added water in coal has been raised by Professor Baskerville. This presents some difficulty, especially in view of the fact that coal is washed in preparation for the market. It might, at first sight, appear that air drying would show whether coal contained an excess of water above its normal amount or not. A consideration of the manner in which the water absorbed by coal will vary with the tension of aqueous vapor of the surrounding air indicates that the only way of determining "added water" would be to find out the percentage of water proper to the coal at the temperature, pressure and tension of aqueous vapor which prevailed at the time of loading, and to compare this with the actual percentage of water.

It is only within certain very wide limits that such a determination would be possible. Dr. Pollard has made some interesting experiments on the question of rehydration of water under varying conditions. It is to be hoped that these and many other matters which have been brought before us by other members may be published separately, as the time and space at our disposal have not allowed us to do them the justice which they may merit, and some of them have only reached us since this Report was well under way.

We feel that the conclusions and recommendations which form the next and the final section of this Report are the reasonable deductions from the facts presented in the body of this Report.

Conclusions and recommendations

The work of the Sub-Committee may be summarized in the following conclusions and recommendations:

1. It does not appear that at present any means exist for distinguishing by analysis between added water "moisture" (which term we take to signify water of adsorbtion; *i. e.*, that

due to a concentration of water on the surface of the particles) and water of crystallisation or of combination, whatever the latter somewhat indefinite term may be supposed to mean.

2. It is probable that the distinction between moisture and water of combination is of little moment in the case of coal, since the losses of water: (*a*) at ordinary temperature under greatly reduced pressure, and in the presence of suitable means for reducing the tension of aqueous vapor to an inappreciable quantity (desiccants), and (*b*) at temperatures a few degrees above the boiling point of water do not differ seriously.

3. Coal is a substance which very readily undergoes oxidation, and the best results in the determination of water are only to be obtained when the coal is treated in an atmosphere containing no oxygen.

4. Coal is a very hygroscopic substance and before being dried, must be properly protected in the laboratory from the effects of changes of temperature or of atmospheric conditions. When dry, it must be protected from any contact with moist air or with moisture in any form until the determination is finished.

5. Unless the initial rate of drying is known to be very rapid, the drying should be divided into two periods of which the latter is much longer than the former. Unless this is done, it is probable that an almost constant small loss, continued over a very long period, may be mistaken for an inappreciable loss.

A consideration of the curve on page 83 will illustrate this point, which obviously applies with very great force to the "vacuum method."

6. When the initial rate of drying is very rapid, e. g. at 105° or thereabouts, the gain of weight by oxidation may *very soon* become greater than any loss due to a very slow rate of drying over a long period.

7. There is no advantage to be obtained by drying coal at temperatures above that of the atmosphere but below, say, 105°C Those who have read the body of the Report or who have even carefully read the above conclusions will not need to be informed that the accurate determination of water in a small sample of coal is a matter of difficulty and requires grave consideration. In the case of large samples of relatively coarse coal, the matter

is of even greater difficulty. We put forward the following recommendations, believing them to be sound, and having due regard to the requirements of both the industrial and the research chemist, but we do not suggest that they are final. We do, however, ask that workers shall give them serious consideration with a view to their adoption.

We recommend that:

1. Whenever possible, especially in the case of very moist coals, the water in the original sample should be determined after it has been subjected to a minimum amount of preliminary mechanical treatment (e. g. thorough mixing with rapid crushing of lumps), by either of the following methods:

(*a*) a carefully weighed portion of from 100 to 500 grams of coal is spread out in a metal tray and exposed for at least 24 hours to the atmosphere of the sampling room. The tray containing the coal is then reweighed and the percentage change of weight is calculated. The coal is then coarsely ground in a mill (a ball grinder is best), and the water determined in the ground portion by one of the methods given in recommendations 2, 3 or 4. The water on the original sample can then be calculated, or

(*b*) the xylene method used by Dr. Constam and given in recommendation 5, all results to be calculated back to the original coal.

2. *For ordinary technical work,* coal should be dried in an oven with a good air circulation for a period not exceeding one hour at a temperature not below 104° nor above 111°C. It is advised that two portions of one gram should be weighed between pairs of accurately fitting watch glasses or in a shallow weighing bottle which have been heated to the temperature of drying and cooled in a good desiccator, and be dried for periods of one-half hour and one hour respectively, the upper glass or the lid of the bottle being removed during the period of drying, at the end of which it should be replaced loosely and the covered vessels placed in the desiccator to cool. At the end of the period of cooling, which should be equal to that allowed for the heated *empty* glasses or bottles, they should be reweighed and the percentage loss calculated. The higher result shall be considered as

the percentage of water in the coal. The required temperature can be obtained by the vapor of boiling toluene (111° C. at 760 mm.), by steam at a pressure of 906–1100 mm. or by an electrically heated thermostatic arrangement. We advise that a long oven with a door in the small end should be used. A toluene oven with a preheating arrangement for the air current, as described by Siaw (*Jour. Soc. Chem. Ind.*, 1911, 61) or other similar device is, in our opinion, a practical arrangement. We strongly condemn air ovens and all devices in which the temperature of the walls of the drying chamber is variable. We believe that a fairly uniform temperature in the whole of the interior of an oven is only to be obtained when the heated walls have an area very largely relative to the cubical contents of the interior and are themselves at a uniform temperature. A preheated supply of air is to be desired. Mere heating without a proper air current is unreliable.

3. Whenever it is suspected that a coal is specially liable to oxidation or the one-half hour and one-hour results differ materially, drying at 104°–111° in a current of nitrogen or carbon dioxide is to be preferred to drying in an oven through which a current of air is passing. Either the direct or indirect method of estimating water may be used. If the former is chosen, care must be taken to prove the dryness of the stream of gas which is passed over the coal. The percentage of free oxygen in this gas must be inappreciable. This method of drying in a current of inert gas is to be preferred for all very exact work.

4. Drying to constant or minimum weight in a vacuum in the presence of sulphuric acid (or other desiccant) possesses no advantage over the last mentioned method. It is very much slower, and, unless the vacuum is very high, it is better to fill the desiccator with carbon dioxide (or other inert gas before exhausting). If this method is preferred, a Hempel desiccator, or any other form in which a large surface of sulphuric acid is exposed both above and below the coal, should be used; the coal should be weighed in watch glasses or shallow weighing bottles and the loss after, say 24 hours, 72 hours and 144 hours, should be taken.

With such prolonged periods of drying, the results obtained by this method are practically identical with those by method 3.

The air admitted into the vacuous space should always be dried by passing slowly through or over sulphuric acid.

5. The method of drying off water from coal by heating in boiling xylene and measuring the water which distils over with the hydrocarbon, is a variant of the method of drying in an inert atmosphere at an elevated temperature. It is worthy of serious consideration and, although we cannot, in view of the limited information at our disposal, recommend it unconditionally, we consider that it is most promising and appears to be particularly suitable for industrial purposes.

6. Coal should always be weighed in closed vessels with well fitting lids or stoppers. Deep vessels such as crucibles are unsuitable for water determinations. Porcelain or metal boats which can be weighed in stoppered or well-fitted sliding tubes may be used.

7. Desiccators with the strongest sulphuric acid which is *frequently* renewed are recommended. If calcium chloride is used it must be ignited before it is put in the desiccator. If phosphoric anhydride is used it must frequently be stirred. These substances are not nearly as convenient or reliable as sulphuric acid.

ANNEXE [1]

HERRN GEORGE-T. HOLLOWAY

Consulting metallurgist, Consulting Chemist, Assayer, London, E. C.

Die mir seinerzeit gesandten Proben Kohle sind Ihren Wunsche gemäss auf den Wassergehalt untersucht worden und zwar:

1) durch Erhitzen im Wassertrockenschrank bei 100°, im Leuchtgasstrom;

2) durch Erhitzen im Wassertrockenschrank bei 100° (in Luft);

3) durch Trocknen im Luftbad bei 105°C (in Luft);
   a) 1 Stunde lang;
   b) 2 Stunden lang;

4) durch Stehenlassen im Vacuumexikkator über Schwefelsäure bis zur Gewichtskonstanz;

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[1] Lettre reçue par M. Holloway postérieurement à la rédaction du Rapport.

Bestimmung des Wapergehalts von 6 Kohleproben (eingesandt von Herrn George F. Holloway, London).

Bezeichnung	Gervichtsverlust im Leuchtgasstrom 100° C.	Gervichtsverlust im Wassertrockenschrank bei 100° C.	Gervichtsverlust im Luftbad bei 105° C.		Gervichtsverlust im Vacuum über konzentrierter Schwefelsäure bei Zimmertemperatur.												
			Nach 1 Stunde	Nach 2 Stunden	Nach 24 Stunden	Nach 48 Stunden	Nach 72 Stunden	Nach 96 Stunden	Nach 120 Stunden	Nach 164 Stunden	Nach 168 Stunden	Nach 192 Stunden	Nach 240 Stunden	Nach 264 Stunden	Nach 288 Stunden	Nach 312 Stunden	Nach 336 Stunden
1	1,41	2,81	3,09	3,06	2,15	"	2,33	2,45	2,54	2.54	"	"	"	"	"	"	"
2	7,59	9,63	9,80	9,82	3.28	'	6,27	7,46	8.11	8,44	8,71	8,91	9,08	9,08		"	"
3	5,42	7,21	7,35	7,19	3,70	"	5,28	5,80	6,03	6,13	6,29	6,49	6,61	6,56	6,56	"	"
4	4,66	5,34	5,62	5,97	1,56	"	2,35	2,93	3,19	3,39	3,63	3,83	4,04	4,09	4,16	4,28	4,29
5	4,40	6,85	7,10	7,06	3,20	"	4,78	5,41	5,71	5,85	6,12	6,26	6,44	6,43	"	"	"
6	5,32	7,04	7,38	7,22	4,25	'	5,62	6,10	6,23	6,33	6,50	6,63	6,73	6,66	6,69	6,80	6.08

Die Ergebnisse sind in beiliegender Tabelle zusammengestellt. Die Zahlen der ersten vier Vertikalspalten sind die Mittel aus je 2–3 Einzelwerten.

Aus den Zahlen der Tabelle ergibt sich:

a) bei 100° im Leuchtgasstrom wurden durchweg niedrigere Resultate erhalten, als bei allen anderen Versuchen. Nach meiner Ansicht gibt das Verfahren unrichtige und zwar zu niedrige Werte;

b) bei Zimmertemperatur im Vacuum über konzentrierter Schwefelsäure wurde erst nach so langer Zeit Gewichtskonstanz erhalten, dass das Verfahren praktisch nicht verwertbar erscheint.

c) die drei anderen Versuchsreihen gaben ziemlich übereinstimmende Werte, die im Wassertrockenschrank in Luft erhaltenen Zahlen sind alle *etwas* niedriger als die bei 105° gewonnenen.

d) zwischen den beiden Versuchsreihen bei 105° ist ein nennenswerter Unterschied nicht vorhanden (bei Probe 4 ist EINER der drei Einzelwerte nach zwei Stunden etwas abweichend).

Es hat demnach keinen Zweck bei 105° länger als 1 Stunde zu trocknen.

Meiner Meinung nach empfiehlt sich dieses Verfahren am meisten.

DR. TH.-WILH. FRESENIUS.

VORSCHLÄGE FÜR EINHEITLICHE BENUTZUNG DER ATOMGEWICHTSTABELLEN

E. Merkel
Nürnberg

Die Internationale Atomgewichtskommission veröffentlicht zur Zeit alle Jahre einen Bericht über den Stand der Erfahrungen der Atomgewichte der Elemente. Diese Arbeit ist zweifellos eine überaus dankenswerte, weil infolge dieses allgemein verrbreiteten Berichts viel sicherer in weite Kreise der Chemiker Kenntnis von den neuen Forschungen auf dem Gebiete der Atomgewichte getragen wird, als wenn diese Ergebnisse nur in den einzelnen Fachschriften als Spezialabhandlungen veröffentlicht werden und nicht in einem zusammengefassten Bericht zur Mitteilung gelangen. Soweit es sich um rein wissenschaftliche Zwecke handelt, ist zweifellos diese jährliche Berichterstattung beizubehalten. Fraglich ist nur, ob es wünschenswert und notwendig erscheint, auch jedes Jahr eine *förmliche Tabelle* mitzuteilen. Der ursprüngliche Anstoss für die ganzen Arbeiten der Internationalen Atomgewichts-Kommission geht von *praktischen* Zwecken aus. Die internationale Atomgewichtskommission hat sich entwickelt durch eine Erweiterung der Kommission der Deutschen Chemischen Gesellschaft, die ihrerseits sich mit der Atomgewichtsfrage beschäftigt hat, auf Anregung der deutschen Kommission für die Vereinbarung einheitlicher Methoden zur Untersuchung der Nahrungs—und Genussmittel und der Gebrauchsgegenstände. Diese letztere Kommission hatte nämlich den Wunsch, mindestens bei ihren Vereinbarungen einheitliche Atomgewichte zu benutzen, und wollte, um die Entscheidung über die richtige Wahl eruf eine etwas breitere Basis zu stellen, den Rat der Deutschen Chemischen Gesellschaft einholen. Es ist dann auch die erste Arbeit der Kommission der Deutschen Chemischen Gesellschaft im Jahre 1898 in den Berichten der Deutschen Chemischen Gesellschaft, Band *31*, Seite 2761 erschienen unter dem Titel "Tabelle der Atomgewichte der Elemente für praktische analytische Berechnungen." Wenn man den ursprünglichen Zweck, dass die verschiedenen Chemiker bei ihren analytischen Berechnungen für praktische Zwecke einheitliche Atomgewichte benutzen sollen, ins Auge fasst, so muss der gegenwärtige Züstand als eine nicht glückliche Lösung der Aufgabe bezeichnet werden. Dadurch, dass die einzelnen Chemiker meist nur mit einer beschränkten Anzahl der Atomgewichte wirklich zu rechnen haben, pflegen sie nicht jedesmal, wenn eine neue Tabelle erscheint, dieselbe auch wirklich in Benutzung zu nehmen, sondern sie rechnen häufig mit den alten Faktoren weiter und es hängt von vielerlei Zufälligkeiten ab, ob und wann ein Analytiker sich einer neuen Tabelle zuwendet. In vielen Fällen rechnen überhaupt die Chemiker mit abgekürzten Atomgewichten, und dies ist, so lange es sich um Analysen innerhalb eines in sich geschlossenen Betriebes handelt, häufig auch durchaus nicht zu beanstanden. Wenn aber Analysen verschiedener Analytiker mit einander verglichen werden sollen, so ist es erforderlich oder doch im höchsten Grade erwünscht, dass den verschiedenen Berechnungen die gleichen Atomgewichte zu Grunde gelegt werden. Die Fachgruppe für analytische Chemie des Vereins deutscher Chemiker ist nun der Meinung, dass sich dieser Zustand viel leichter und sicherer erreichen lässt, wenn man nicht alle Jahre eine förmliche Tabelle veröffentlichte, sondern wenn dies nur in Intervallen von etwa 5 Jahren geschähe, und wenn dann, auf Grund einer internationalen Vereinbarung, man sich darauf berufen könnte, dass in dem gegenseitigen Verkehr diese Zahlen von einem *bestimmten Datum an* zur Benutzung kommen sollten und allgemein als massgebend anzusehen seien. Der Einwand, dass man dann etwa eine erhebliche Aenderung eines Atomgewichtes längere Zeit hindurch von der praktischen Anwendung ausschliesst, dürfte nicht sehr ins Gewicht fallen, weil wir doch einerseits damit rechnen müssen, dass erhebliche Aenderungen bei den Zahlen der wichtigeren Elemente nicht sehr wahrscheinlich sind und auf der anderen Seite die Bestimmungen, unter denen die Analysen in der Praxis ausgeführt werden, von denjenigen *der* Versuche, aus denen die Atomgewichte abgeleitet werden, recht verschieden zu sein pflegen, so dass es an und für sich überhaupt zweifelhaft ist, ob man mit der Anwendung richtigerer Atomgewichte wirklich auch aus den Analysenergebnissen die gesuchten Bestandteile zutreffender auszurechnen in der Lage ist. Für den Fall, dass, wie der Verein deutscher Chemiker beantragt hat, die Internationalen Kongresse in Zukunft nur alle 5 Jahre abgehalten werden sollen, würde sich empfehlen als Zeilpŭnkt von dem an die neuen Tabellen zur Anwendŭng und allgemeinen Anerkennung kommen sollen den 1. Januar *des* Jahres zu wählen, welches auf die Abhaltung eines Internationalen Kongresses folgt. Sollte der Beschluss, die Internationalen Kongresse nur alle 5 Jahre abzuhalten, *nicht* gefasst werden, so würde sich empfehlen, etwa vom 1. Januar 1915 ab zum ersten Male die in Herbst 1914 veröffentlichte Tabelle als allgemein giltig zu bezeichnen.

Wenn die Sektion für analytische Chemie des Internationalen Kongresses bei ihren Beratungen dem Antrag zustimmt und ihm ihrerseits empfehlend an die Leitung des Gesamtkongresses weitergibt, und wenn der Gesamtkongress seinerseits den Antrag billigt, so würde weiter Seitens der Kongressleitung an die internationale Atomgewichts-Kommission mit der Bitte heranzutreten sein, zwar alle Jahre über die Forschungen auf dem Gebiete der Atomgewichte zu konferieren, aber nur alle 5 Jahre eine förmliche Tabelle für den praktischen Gebrauch zusammenzustellen. Es würde sich dann natürlich auch als notwendig erweisen, solche Hilfswerke, wie die Rechentafeln von Küster, die gegenwärtig alle Jahre erscheinen, nur immer in Zeiträumen von 5 Jahren herauszugeben, so dass sie von dem betreffenden Datum an immer nur in der neuen Auflage zur Benutzung kämen. Es ist nicht zu erwarten, dass etwa nun der Absatz solcher Rechentafeln dadurch kleiner würde, denn Küster berichtet selbst im Vorwort seiner letzten Ausgabe die auch von anderer Seite mehrfach konstatierte Tatsache, dass sehr häufig Rechentafeln, die viele Jahre alt sind, sich noch im Gebrauch befinden. Gegenwärtig wird sehr häufig der Wechsel weniger davon abhängen ob neue Atomgewichte festgestellt worden sind als davon, wann die Rechentafeln abgenutzt sind. Dass hierbei naturgemäss die einheitliche Benutzung derselben Atomgewichte nicht gewährleistet wird, liegt auf der Hand.

REPORT OF THE COMMITTEE ON STANDARD METHODS FOR DETERMINING SMALL HYDROGEN-ION CONCENTRATIONS

The Committee appointed by the President of the Section of Analytical Chemistry to consider the advisability of recommending to the Congress that provision be made for coöperative investigations of standard methods of determining small hydrogen-ion concentrations respectfully presents to the Section of Analytical Chemistry the following report.

The Committee considers that the problem is one which involves several factors, each one of which requires more thoro experimental investigations before standard methods can be decided upon. Of these lines of investigation one of the most important seems to be the determination of the extent to which different methods of obtaining standard solutions of definite hydrogen-ion concentration give concordant results. Such solutions may be prepared with the aid of mass-action calculations by mixing various weak acids or bases with their neutral salts, or by using hydrolyzed salts of weak acids or bases, or acid salts of polybasic acids. These calculations involve an accurate knowledge of the ionization-constants of the acids and bases in question and of that of water itself, as well as the validity of the mass-action principle.

Another method of fixing small hydrogen-ion concentrations consists of measuring the electromotive force of a hydrogen-gas cell containing at one electrode the solution to be investigated. This method involves certain theoretical difficulties, especially the question of the validity of the ordinary electromotive force equation, and the estimation or elimination of the "liquid-potential" between the two solutions.

Since it is most convenient to employ acidimetric indicators for comparing the hydrogen-ion concentrations of various solutions, the problem also involves a thoro study of a number of indicators sufficient to cover a range of hydrogen-ion concentrations from 10^{-3} to 10^{-11}. This study should include experimental determinations of the proportion of each indicator transformed into its salt in solutions of various hydrogen-ion concentration, and also in solutions containing neutral salts at various concentrations, since these have been shown to have a large effect on many indicators.

This brief statement of the problem will serve to show that it is a comprehensive one requiring much experimental work as a preliminary to a satisfactory solution. As a means of bringing to the attention of chemists the desirability of undertaking investigations in this direction the committee suggests that this report be printed in the Proceedings of the Congress. It does not recommend that a permanent committee be appointed at the present time, for the reason that the available data are not yet sufficient to justify such a Committee in proposing even provisional standards for determining small hydrogen-ion concentrations.

A. A. NOYES.
G. P. BAXTER.
H. N. MCCOY.
JULIUS STIEGLITZ.
E. W. WASHBURN.

THE DETERMINATION OF ZINC BY ELECTRO-ANALYSIS

ELLWOOD B. SPEAR AND SAMUEL S. STRAHAN
Massachusetts Institute of Technology, Laboratory of Inorganic Chemistry

The electrolytic determination of zinc has been attended by unsatisfactory results because many of the vital conditions were not known and many of the causes of deleterious effects not clearly understood. Two years ago an article was published[1] by one of us on the causes of the high results so frequently obtained and in another article[2] the statement was made that our experiences with the potassium and sodium hydroxide methods were unsatisfactory. Some time later Kemmerer[3] published very fair results having used a rapid method with KOH. This method is, with the slight modifications we have introduced, one of the very best for the determination of zinc.

Our modifications consist, first; in cooling the solution a few minutes before the end of the experiment, and second; in reducing the amount of the KOH employed. The reasons for these changes are discussed below. We have also carefully investigated the various causes of error in the employment of this method. These causes will be considered later, the procedure itself is as follows.

The zinc to be determined, preferably about 0.4 gm. must be in the form of sulfate. Nitrates and ammonium salts must be absent. Very little free sulfuric acid should be present because potassium sulfate, which is formed when the acid is neutralized with the hydroxide, is not very soluble in strongly alkaline solution. 10–25 gms. KOH are dissolved in water and the total volume of the electrolyte made up to 125 cc. The solution is brought almost to the boiling point and electrolized with a normal current density of 3 amperes. A rotating platinum anode and stationary nickel gauze cathode may be used but we strongly recommend a rotating nickel gauze cathode (see fig. 1) and a stationary platinum plate or spiral anode. The cathode must be kept completely buried in the solution. The anode should be placed above and never at the side of the cathode. The time required for complete precipitation varies, of course with the size of the cathode. With a cathode area of 100 sq. cm. the time necessary was 45 minutes using 25 gms. KOH, and 30 minutes using only 12 gms.

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[1] Journal of The American Chemical Society, *32*. 533.

[2] Journal of The American Chemical Society, *32*. 532.

[3] Journal of Industrial and Engineering Chemistry, *2*. 375.

7–8 minutes before the end of the experiment the anode and the inside of the beaker should be washed down with a small amount of water from a wash bottle in order to obtain any zinc that may have crept up owing to frothing or stirring. This is a precaution that should always be taken in electroanalysis.

5–6 minutes before removing the electrodes the solution should be cooled, with ice if necessary, to below 25° C. The solution should be lowered from the electrodes without interrupting the current. The cathode should be quickly but thoroughly washed first with water, then with alcohol and finally with ether that has been very recently dried over sodium and freshly distilled. The ether should be immediately dried off the cathode by gentle heating and the electrode weighed after standing for one half hour in a dessicator.

The method is capable of giving very good results but this is due to a compensation of errors. When the deposit is washed with water some zinc is always lost in the wash water while some zinc hydroxide is formed at the same time on the electrode. These two amounts are small and very closely counter balance each other. In tables 1 and 2 we give 16 consecutive results using 25 and 12 gms. KOH respectively. The results were not all obtained on the same day nor by the same experimenter.

TABLE 1

No.	Amt, taken	Amt. found
1.	0.3946	0.3943
2.	"	3948
3.	"	3949
4.	"	3947
5.	"	3949
6.	"	3955
7.	"	3945
8.	"	3942

TABLE 2

No.	Amt. Taken	Amt. Found
1.	0.3946	0.3946
2.	"	3948
3.	"	3952
4.	"	3952
5.	"	3950
6.	"	3943
7.	"	3947
8.	"	3951

Preparation of the Solutions for the Investigation

Zinc sulfate:—About 4 gms. C. P. zinc, the purity of which had been varified by a careful analysis, were dissolved in nitric acid, slightly more than the requisite amount of concentrated sulfuric acid was added and the whole evaporated to dryness over a water bath. The resulting zinc sulfate was dissolved in water and the solution made up to 250 cc. in a carefully calibrated flask.

Potassium hydroxide:—250 gms. KOH of good quality were dissolved in water and the solution made up to one liter.

Solution for analysis:—25 cc. of the zinc sulfate solution from a carefully calibrated pipet were added to 100 cc. of the prepared KOH in a deep 250 cc. beaker. For the analyses using a lesser amount of KOH 50 cc. of the solution and 50 cc. water were taken. The solution was brought almost to the boiling point and at once electrolized. Zinc deposits from hot KOH have a much more metallic appearance than those from cold solution and in the latter case the results are always too high. The solution must not contain nitrates else all the zinc cannot be thrown down. One gram of potassium nitrate will almost completely prevent the deposition of the zinc. We have not yet investigated the cause for this.

THE ELECTRODES AND THEIR MANIPULATION

Cathode:—Many copper, platinum and nickel cathodes of various shapes were tried and the most satisfactory was found to be one of our own design as shown in Fig. 1. It is made of nickel gauze, 30 mesh to the inch with a stout wire standard of the same material. The gauze should not continue to the centre to meet the stem because the rotating motion given to the solution sometimes causes the centre to become exposed to the air and some of the freshly deposited zinc is oxidized to zinc hydroxide. If zinc is deposited electrolytically and any portion of the deposit is exposed to the air a white ring of zinc hydroxide can be seen on the upper edges. Our investigations showed that the deposit always weighs 2–4 mgs. too much, provided that the cathode protruded above the solution. This fact doubtless explains some of the high results obtained by many experimenters.

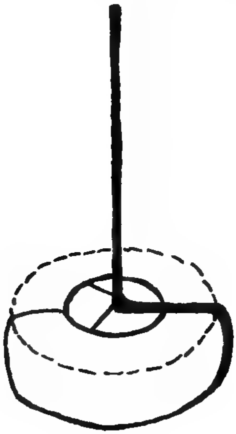

FIG. I.

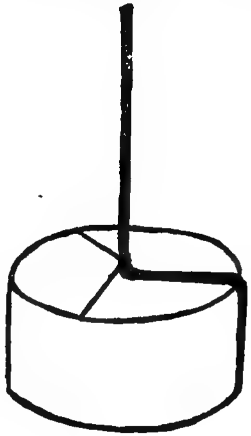

FIG. II.

The upper edge of the cathode should be turned in toward the centre for, as the anode is placed above the cathode for reasons given below, most of the deposition will take place on the extreme upper edge, become bad and fall off if the cathode is shaped as shown in Fig. 2. The cathode was rotated at the rate of 400 revolutions per minute. A rotating cathode is preferable to a rotating anode because in the former case a much better stirring effect on the immediate surface of the cathode is obtained. Copper cathodes are not suitable because they oxidize somewhat in hot solution and thus introduce an error. Platinum cathodes do not give so good zinc deposits as nickel possibly because of the difference in polarization effects on these two metals.

Anode:—As already indicated the anode may be a platinum plate or spiral. The object in placing the anode above the cathode is to prevent the oxidation of the deposit by the gases liberated by the current. It was found by experiment that the rate of deposition was very much slower, and that it was almost impossible to get all the zinc out if the anode were placed by the side of and close to the cathode. This is an excellent confirmation of the theory pointed out by one of us in an article in these proceedings on oxidation processes at the cathode.[1]

The solution should be cooled for the last 5–6 minutes, with ice if necessary, in order that the temperature of the liquid may not be above 25 C. when the cathode is removed. At the moment of lowering the solution the cathode is covered with a layer of KOH which rapidly attacks the deposit if the temperature is above 25 C. Some of the zinc would be dissolved and potassium zincate be formed. When the cathode is washed most of this comes off and zinc is thus lost in the wash water. Even when the temperature is low some zinc is found in the washings but the amount is fortunately small. On the other hand the solution must not be cooled too long before the end otherwise the character of the deposit is affected.

The cathode must be washed thoroughly by rotating it in water to get rid of the KOH. The water should be cold and the work should be done with despatch or an appreciable amount of zinc hydroxide will be formed thus invalidating the determination. The deposit should next be dipped into alcohol and finally thoroughly wet with ether that has been dried over sodium. Washing with alcohol and ether alone will not remove all the KOH, and the results will be high if water is not used. The deposit should be immediately dried over a heated surface or free flame.

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1. The Coprecipitation of Copper and Carbon by Electrolysis; Oxidation at the Cathode. These Proceedings, Secton 10a, Electrochemistry.

The ether must not be allowed to evaporate off in the air nor in a dessicator else the metal, cooled below the temperature of the surroundings, will be covered with a film of moisture that will attack the deposit, form zinc hydroxide and therefore increase the weight. This was shown experimentally by treating the previously dried and weighed deposits with ether, allowing them to stand in a dessicator until dry and reweighing. Each treatment caused an increase of from 2–6 tenths of a millegram. It is unwise to heat the deposit much above the temperature of the surroundings. If the ether is not recently dried and distilled it contains water and oxides that attack the freshly deposited zinc.

It is obvious that the naked cathode should be treated in precisely the same manner before the electrolysis in which the deposit is to be when the precipitation is completed.

The endeavor was made to prevent the loss of zinc in the wash water first, by syphoning off the KOH solution and gradually replacing it with water; and second, by making the wash water a conductor with a few drops of KOH and allowing the current to pass through while the cathode was being washed. The first method proved a failure because zinc is continuously redissolved even during the passage of the current. A portion of this zinc was unavoidably syphoned off and lost. Employing the second method we succeeded in getting all the zinc on the electrode but the results were invariably from 2–4 mgs. too high. This increase in weight was doubtless due to the presence of zinc hydroxide formed by the action of water on the deposit.

Our investigations embraced a large number of experiments and 180 quantitative determinations.

SUMMARY

In this article we have introduced certain modifications of the potassium hydroxide method and shown that it is reliable for the electrolytic determination of zinc.

We have shown that this method entails a compensation of errors.

A new cathode has been devised and recommended for use in electroanalysis.

The following sources of errors have been investigated and pointed out:

1. The loss of zinc in the wash water, counterbalanced by the formation of zinc hydroxide on the cathode.
2. The effect of air on an exposed cathode.
3. The oxidation of the deposit by anode gases.
4. The effect of temperature at the beginning and end of the electrolysis.
5. The effect of ether containing water and oxides on the deposit.
6. The high results obtained by letting the ether evaporate off the cathode in a dessicator.
7. The presence of nitrates.

THE PRODUCTION OF CHLORINE SUBSTITUTION PRODUCTS OF METHANE FROM NATURAL GAS[1]

CHARLES BASKERVILLE AND H. S. RIEDERER.
College of the City of New York, New York, N. Y.

One of us (C. B.) has discussed elsewhere[2] the attempts which have been made to effect a chlorination of methane in order to obtain satisfactory yields of substitution products. It may be noted here that while the formation of methyl chloride, dichlormethane, chloroform and carbon tetrachloride from methane has been experimentally shown by several investigators operating with various methods, and a number of processes have been patented for the production of these and other halogen derivatives of methane[3] so far no process has been worked on a commercial scale. Since there is an abundance of natural gas containing 50–90 per cent. methane produced in this country, the problem is of some importance,—one which we thought would bear investigation along lines differing in certain respects from those hitherto followed.

In general, it may be said that the ultimate object of those studying the matter has been to produce a constant yield of an intermediate product. Bearing in mind the demonstration of Phillips,[4] that the tendency of methane when chlorinated, is to constantly produce either methyl chloride or carbon tetrachloride, it occurred to one of us (C. B.) that it would be more advantageous to obtain the end product, from which, among other products, chloroform could be prepared by reduction.

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[1] The authors have filed applications for patents on the novel features presented in this paper.

[2] J. Ind. Eng. Chem., *4*, 216 (1912).

[3] Mallet, U. S. Patent 220,397, October 7, 1879; Colin, U. S. Patent 427,744, May 13, 1890; Elworthy and Lance, French Patent 353,291, May 15, 1905; Mackaye, U. S. Patent 880,900, March 3, 1908, and 1,009,428 November 21, 1911; Walter, German Patent 222,919, November 5, 1909; and Pfeifer and Szaroasy, 12,058, D. Anm. P. 24,872, Sept. 25, 1911.

[4] Am. Chem. J., *16*, 362.

Accordingly a number of experiments were conducted with a view of devising a commercial process for the production of carbon tetrachloride from natural gas.

EXPERIMENTS WHEREIN A SPARK DISCHARGE WAS EMPLOYED

In preliminary experiments, an apparatus similar in principle to that used by Phillips, was employed. It was finally decided, however, to construct an apparatus with a closed circuit, producing a circulation of the gases by heat on the rise, cooling on the drop, and recovering the products in a trap at the bottom; suitable openings to be made in the apparatus for the introduction of chlorine and natural gas, and for the insertion of spark terminals in such a manner as to bring the spark in the junction line of the gases. The apparatus constructed along

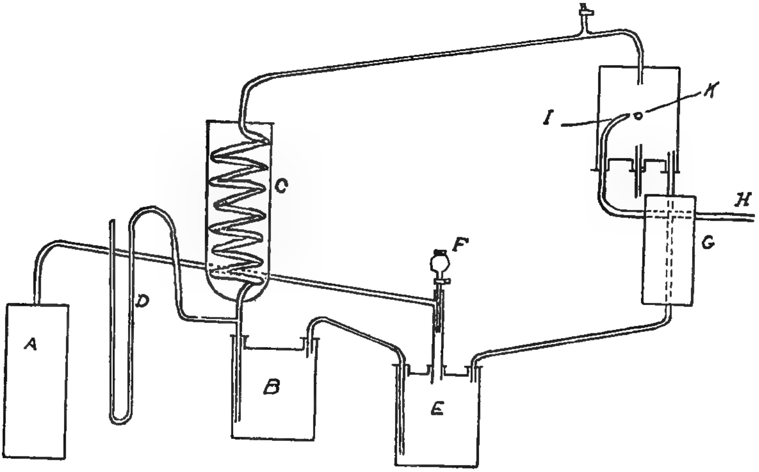

Fig. 1.

FIGURE I.

A, Chlorine cylinder; B, receiver for substitution products of the reactions; C, condenser; D, pressure gauge; E, hydrochloric acid absorption chamber; F, funnel for introducing water; G, electric heater; H, tube for introducing natural gas, which plays between carbon spark terminals K; L, cock for releasing pressure.

these lines is illustrated herewith (Figure 1.) Several modifications were made in this apparatus during the course of the experiments, and in the later experiments a horizontal reaction chamber (Figure 2) provided with a glass pocket for the collection of any condensation products in a liquid form and with a hollow carbon terminal for the introduction of the natural gas[1] was used. In the experiments wherein this form of reaction chamber was used, just as in the case of the original form of chamber, bridging between the carbon terminals invariably occurred, although combustion ensued almost immediately upon starting the spark. A very small yield of products was obtained.

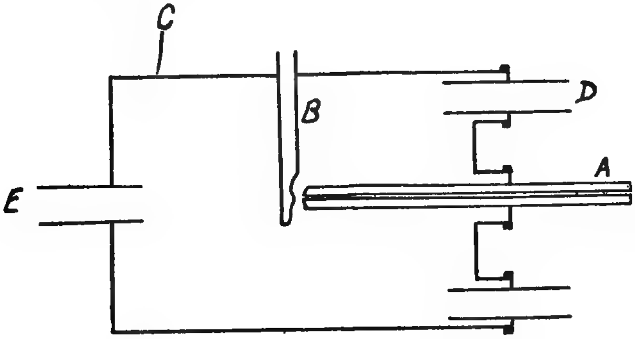

Fig. II

FIGURE II.

A, hollow carbon transmission tube for natural gas; this carbon is one terminal; B, solid graphite spark terminal; C, reaction chamber of glass; D, chlorine inlet; E, exit for gaseous products of reaction.

The first three runs, using the original form of apparatus, showed that chlorine substitution products could be obtained, although the character of the products could not be determined owing to the small yields. The spark in these runs generally showed a dual character, partly resembling an arc and partly presenting the true color of a spark. Undoubtedly there were considerable ultra violet rays in this latter portion.

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[1] Besides natural gas, methane, prepared by various methods, was used in preliminary experiments. In the following experiments, however, natural gas alone was used.

In the runs, using the reaction chamber illustrated in Figure 2, the spark showed little of the deep blue and more of the flame. Since the gas was continuously directed into the spark, it burned continuously.

In the first three runs it is doubtful if the flow of natural gas was continually into the direct line of the spark, as no continuous flame was observed as in the runs with the modified apparatus, and it seemed reasonable to conclude that whatever chlorination was effected was through the agency of the ultra-violet rays and not by the combustion.

In all of the above experiments natural gas saturated with water was introduced into the circulating atmosphere of chlorine.

EXPERIMENTS WHEREIN ULTRA-VIOLET RAYS WERE UTILIZED

The apparatus used in the experiments which follow next was constructed as shown in Figure 3. The reaction chamber was a cruciform tube of glass, through two opposite components of which was inserted a quartz tube containing iron terminals.

In beginning, the apparatus was folled with chlorine, the heat and the spark started, and then natural gas (80–90 per cent. methane) was admitted. The pressure variations showed that a reaction occurred, but no product could be observed except a crystalline film suspended on the water in the receiving vessel. About 5 liters of natural gas were used. Even after continuing the run for 8 hours, during which time 3½ liters of natural gas were used, no appreciable product was obtained. Accordingly the apparatus was changed so that the natural gas was admitted below through the U-tube intended for a drain, causing it to bubble through the hydrochloric acid in the receiver.

In the next experiment, a considerable quantity of product collected in the receiving vessel. 7½ liters of natural gas were used and the temperature of the heater was maintained so low that no vapors were observed in the rising tube above the furnace. After another run, in which 3½ liters of natural gas were used, the apparatus was disconnected and the product was separated

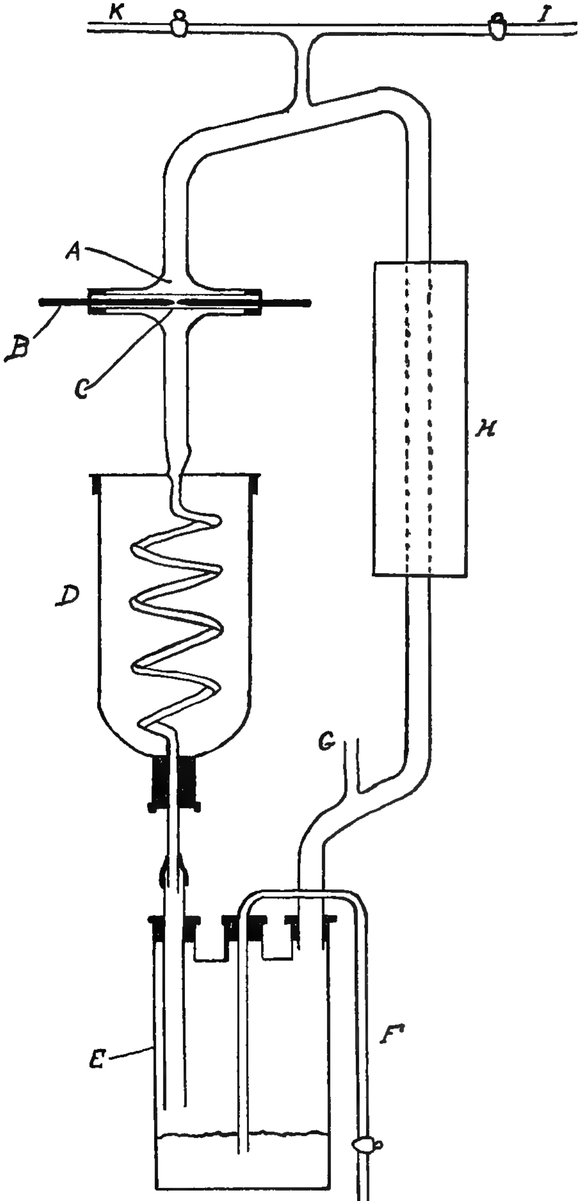

FIGURE III.

A, cruciform glass reaction viaduct; B, iron terminals; C, quartz tube containing iron terminals; D, condenser; E, receiver; F, syphon for emptying receiver; G, chlorine inlet; H, electric heater; I, natural gas inlet; K, connection to manometer.

from the hydrochloric acid in the receiving vessel. 10 cc. of product were obtained, this was purified and fractionated. The first fraction came over at about 64 deg. C., and the fractions up to 76 deg. C. were collected. A second fraction was then taken up to 88 deg. C. and a residue remained in the fractionating bulb. The first and second fractions were colorless and clear, while the residuum possessed a yellow color. The first fraction amounted to about 75 per cent. of the total, the second and the residue to about 12.5 per cent each. These experiments showed that approximately a 20 to 25 per cent. yield of carbon chlorides (chloroform and carbon tetrachloride) could be obtained from natural gas, using a circulating atmosphere of chlorine in the apparatus described.

In the succeeding experiment the apparatus was made absolutely air-tight and a thermo-electric couple was introduced into the furnace to enable temperature readings. A run was made *without* a spark. Preliminary experiments showed that but a slight reaction occurred and that the crystalline product (hexachlorethane) formed was inappreciable, although very little natural gas was used; accordingly no further experiments were made without a spark with this apparatus.

In the following run, which lasted for 8 hours, considerable product collected, and the yield seemed to be in proportion to the natural gas used. The next runs were made after sweeping the apparatus with chlorine. After natural gas and chlorine were both added, the reaction proceeded smoothly and it was finally stopped by admitting chlorine alone. The product amounted to 14 cc. from about 10 liters of natural gas; this was purified and fractionated, and was found to consist of carbon tetrachloride and a small amount of chloroform and hexachlorethane.

From the next experiments, an outlet siphon for the hydrochloric acid produced and an inlet tube for natural gas were provided in the receiver. The apparatus was completely filled with chlorine, but no heat was used in the circuit. About 4 liters of natural gas were used in each run, and considerable product was obtained; the product was not separated owing to the fact that it was in part distributed throughout the apparatus. It

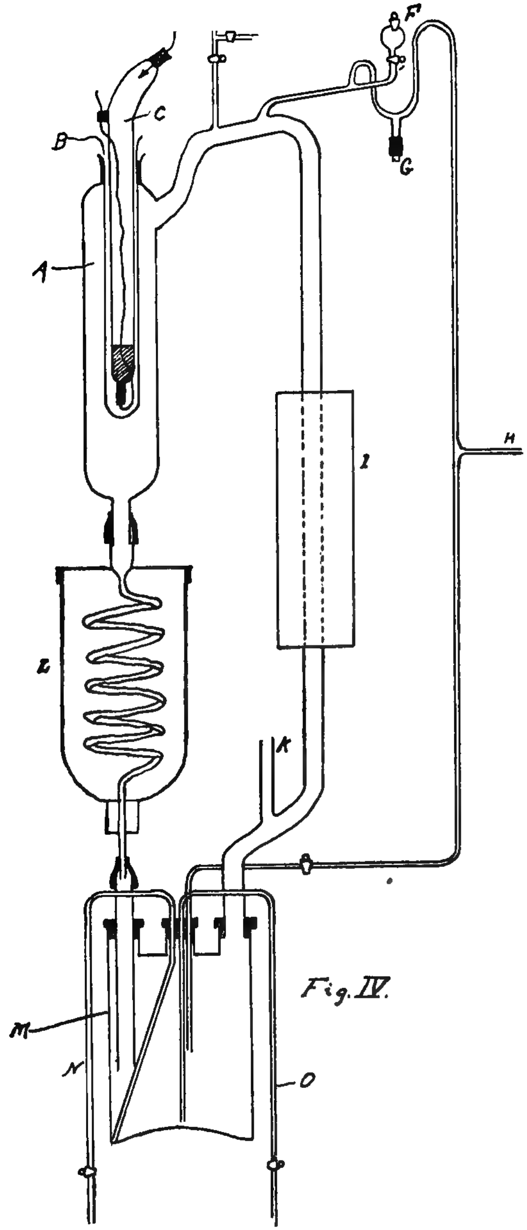

FIGURE IV.

A, Reaction chamber of glass; B, large thin walled quartz tube; C, Uviol lamp inserted after current is started; D, tube connection to manometer; E, cock for releasing pressure; F, funnel for introducing water; G, trap; H, tubes for introducing natural gas before or after the heater, I; K, chlorine inlet; L, condenser; M, receiver; N, syphon for removing heavy products of reaction; O, syphon for removing water solution of hydrogen chloride produced in the reactions.

was determined that the product is very sparingly soluble in hydrochloric acid and chlorine water. Attempts were made to ascertain whether the ultra-violet rays have any influence on the reaction between chlorine and methane. Beginning with daylight, the ultra-violet source was then started and observations were made on the speed of the reaction. As in the preceding experiments, the issuing natural gas was saturated with water by passage through a water bottle. However, the variations in pressure were not sufficiently marked to lead one to infer that the ultra-violet rays have any effect on the reaction. In order to definitely establish this fact, a reaction chamber was constructed to accommodate a "Uviol" lamp to replace the spark section. Provisions were also made for exposing, or not exposing, the mixed gases to ultra-violet light, depending upon what was necessary to produce a reaction, for drying the gases by passage through sulphuric acid after the separation of the products of chlorination; and for passing the residual gases over quick-lime, the form of apparatus used is shown (Fig. 4).

Beginning with a full charge of chlorine, the apparatus was run for one day and no appreciable reaction could be observed. From the experiments made, it seemed probable that the ultra-violet rays are not the necessary active rays required, for it was found that the reaction occurs in daylight, and the passage of the solar rays through glass would exclude ultra-violet light. From the observations made so far, it appeared that the solution of the problem was to find the proper rays. Therefore, the "Uviol" lamp was removed and the aperture closed.

A tungsten filament lamp was mounted outside of the reaction chamber, surrounded by a reflector, and no appreciable reaction occurred, although runs were made under varying conditions. Using an incandescent gas mantle containing 10 per cent. of ceria, whereby the proportion of red rays was increased, with and without the aid of daylight, the reaction was practically *nil*, while with a mantle containing 3 per cent. of ceria only a slight reaction occurred. With the 3 per cent. ceria mantle, the reaction would take place when daylight was admitted, but would practically cease in the dark. At times a slight reaction was noted when working in the dark, but this was attributed to diffused light entering through the laboratory door.

In the next series of experiments a projection lantern, using only one condenser lens and ordinary carbons, was placed in such a position as to light the upper section of the reaction chamber. The lantern was run on an 8 ampere 235 volt current, and it was shown conclusively that the arc light causes the reaction to take place. Colored screens were then interposed between the lantern and the reaction chamber, and in this manner the rays favoring the reaction were determined. A spectroscopic examination of the screens (solutions of coal tar dyes, blue, green, red and yellow such as are used in the Pinatype color photography outfit) showed that the blue screen passed through the green and gave but a dim indication in the deep red; and that the green cut out every ray except the green with a blue fringe; and that the yellow and red screens excluded the blue end of the spectrum along with part of the green. A number of experiments demonstrated that the unscreened arc light and the arc light screened with the blue allowed a good reaction speed, while the interposition of the green, yellow and red screens slowed down the reaction almost immediately and to a considerable degree; on replacing the blue screen, however, the reaction was at once accelerated. It was found that it made little difference whether chlorine or natural gas was being run into the apparatus, except that the character of the product varied accordingly. Further experiments showed that the blue end of the spectrum is the active agent for the reaction of chlorine and natural gas. It was found that screening is of little use, since the inactive red, yellow and green rays are hardly of an interfering character. The primary important condition was found to be a source of light rich in the rays of the visible blue spectrum, that is, the spectrum from the bluish green through the visible violet. We have found that the invisible spectrum (the ultraviolet) does not induce the desired activity and that it plays little part in the reaction.

As it was not always convenient to fuse the large glass tubes in making connections, it may be of interest to give the method resorted to for making tight junctions through which such corrosive gases as chlorine and hydrogen chloride may be passed. The glass tubes are first cut smooth and closely fitted to each other. The junction is then wrapped with wet thin sheet of asbestos paper. After drying the asbestos is given several coats of Bakelite varnish No. 4. The next day this is tightly wrapped with electric adhesive tape and thoroughly coated again several times with the Bakelite varnish.

ACTION OF SOME FLUORINE COMPOUNDS ON CLAY, WATER, ETC.

D. H. Childs
Buffalo, N. Y.

Addendum to Volume II, p. 67.

Since writing the paper as printed in Vol. II, p. 67, the following observations were made.

Absorption of Hydrofluoric Acid Gas

Gas run for one hour, as usual, through the tower, which was thoroughly rinsed afterwards, the rinsings containing the acid.

Tower filled with coke, wet with water, no water flowing.

Air	4.9 cu.ft.
Time	1 hour.
N. Alkali used	29 cc.

Same conditions, except Green Clay in tower in place of coke.

N. Alkali used	38.3 cc.

Elimination of Silica by Hydrofluoric Acid Gas

Lump clay was heated in an iron crucible, and the gas passed over. Before passing the gas the clay was heated for the time and at the temperature shown below. The attached notes show the results:

	Before gassing.	After gassing.
Time	75 minutes.	A few minutes. Silica blown over, clogging the tube.
Temperature	250°C.	250°C.

Second Run. Using the same clay.

Time		1 hour. Heavy deposit of Silica in Bakelite tube which carried gas to the water.
Temp		240°C. Fluor Spar used to make acid. Acid caught 3.6 cc Normal.

Third Run. New lot of clay.

Time	55 minutes.	35 min. Silica ring formed as before in tube.
Temp	140°C.	145°C. Fluor Spar. Acid caught 17cc. N.

Fourth Run. Some Clay from first run used. Clay placed in Pt. crucible, and heated to 250°C., HF made from Ammonium Fluoride free from silica used. Sample taken, 4.2 g.

Wt of Crucible and sample before gassing	16.1895 g.
" " " " " after "	15.900
" lost in the HF treatment	.2895
Loss on Ignition of original material on which this run was made	12.41%
Loss on Ignition after the HF treatment described above, based on weight before treatment	15.53%
Loss during HF treatment	6.82%

Heating a Mixture of Clay and Aluminum Fluoride

10 g. China Clay,
23 g. Fluoride.

These were well mixed and a sample of 5 g. taken in a platinum crucible. It was heated for periods of 45 minutes each and weighed. Air was passed over to carry off any acid or water that might distill. In the one set steam was lead over with the air. I think the temperatures are more accurately determined in this series than in the one when the temperature of decomposition of the fluoride was tested. At point marked XX a trace of acid was shown in the gases coming out by smell and by absorption in water.

No Steam		With Steam	
Temperature	Loss in weight	Temp.	Loss in weight
120°C.	0.1335 g.		
185	.4245 g.		
250	.2135 g.	210°C.	0.688 g.xx 1 hour
450	.1370 g.xx	450°C.	.199 g. 55 min.
700	.2600 g.		.3 cc N. alkali in both cases
700	.1210 g.25min. extra		
900	.1970 g.		
1100	.7250 g.		

The 900° was estimated from color, being a bright red one half way up; the 1100° was over a blast-lamp which would not melt copper in a small porcelain crucible in an hour, nor would two such lamps.

SUMMARY

These notes show that the absorption is greater when the tower is filled with clay than when coke is used; that silica is eliminated at the low temperature of 140°C. by passing HF gas over the clay; that the reaction is much more rapid at about 1000°C. than at lower temperatures, possibly because the work done the HF came off more rapidly at that temperature; that steam does not appreciably hinder the loss in weight, when the time is taken into consideration, (though whether this loss is silica or HF does not appear, except that the amount of acid caught was small).

In an attempt to find the conditions for equilibrium in the system Water-Silicon Fluoride-Hydrofluoric Acid-Silica a tube was set in a heating chamber, some Silicon Fluoride passed in, 0.12 g. water added, the tube connected to a gas burette and as the gas was heated the pressure was kept constant and the volumes read, or rather the increase of the volume. The volume of the tube was determined by Boyles law, and the volume the gas would have occupied if there had been no chemical action was calculated on the basis of the space heated containing as much water vapor as it would have contained had it been at the temperature of the burette outside the heater. In support of this assumption it may be said that water collected in the tube just outside the heating chamber. The curves resulting from these observations are not yet completed to my satisfaction, and I do not wish to do more than to mention some of the points to be noted:

I. In one curve a very decided break in the curve at 110°C. where it stopped its rapid increase in volume for a time. In another attempt where a larger amount of water was used the break came at 107°C., these breaks corresponding to the boiling points of those solutions, presumably.

II. When the gas mixture was heated rapidly the volume attained seemed to be the same as when the heating was slow, while on rapid cooling the volume was much greater than it had been at the corresponding temperatures during heating. On slow cooling the volume was the same as on heating to the same temperature. This may be due to the small amount of silica present, it being solid.

III. In accord with Le Chatelier's rule, the reaction is seen to proceed toward the HF plus Silica side as the heating is continued.

Mention was made to the writer of a statement to the effect that in presence of the fluorides iron is more rapidly changed from ferrous to ferric. To test this point solutions were made up containing ferrous iron and in half of them some ammonium fluoride, and in all excess of sulphuric acid. These were tested in pairs with potassium permanganate, and no difference found, although one pair was left 24 hours before titration, and was heated for half an hour to 50°C., with shaking.

In closing, allow me to express my thanks to Dr. W. G. Wilcox, of the National Carbon Co., Cleveland, Ohio, for his assistance in the analysis of the problem before me.

ALUMINA, HYDROCHLORIC ACID, CAUSTIC ALKALIS AND A WHITE HYDRAULIC CEMENT BY A NEW PROCESS FROM SALT, CLAY AND LIME

Alfred H. Cowles
Sewaren, N. J.

Since 1862, or earlier, the proposal has been in the literature to produce hydrochloric acid and potassic or sodium compounds from salt and clay by passing steam over the mixture at a high temperature.[1] These proposals have all been condemned as impracticable by Thorp's Dictionary, Lunge and other high authorities.[2]

It was not until 1902 that a method was patented by Adolf Kayser to effectively and economically separate the silica from an alkali-silico-aluminate formed as one product in the above process.[3]

From another cause, the attempts to render this process a success when carried out on a commercial scale, resulted in failure. Namely; if moist clay and salt alone be mixed together, moulded in the form of perforated briquetts, and after drying, be heated to a good red heat, but not high enough to melt the final product; and vapor of water be passed through the mass, a chemical action begins on all surfaces of each heated briquette. The vapor of water gives oxygen to the sodium of the salt, and hydrogen to the chlorine, thus hydrochloric acid passes off as a vapor, while sodium monoxide combines with the silica and alumina of the clay, forming sodic-silico-aluminate. This action slowly passes inward from the surfaces of all heated briquettes. The conversion of the material from the outer surfaces inwards is slow. Kayser, in the nineties found that it took seventy-two hours for the change to penetrate through a briquette wall, from its two sides, that was scarcely more than one-half an inch in thickness, and this in a furnace capable of containing many tons of such material. Here is one of his briquetts. It has a crystalline structure. Though shrunken some, it retains its moulded form.

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[1] English patent No. 2050 A. D. 1862 of William Gossage. English patent No. 2679 A. D. 1874 of Herman Gruneberg and Julius Vorster. A number of American patents to Adolf Kayser between the years 1886 and 1896, also English patent No. 11492 to Adolf Kayser.

[2] Lunge Vol. 2 page 429, 1895 Edition. "*Heating sodium chloride mixed with clay in a current of steam* according to Vorster and Gruneberg, produces sodium silicate and steam (?) The temperature is so high and the wear and tear of the apparatus so great, that this process is not practicable."

Thorp's Dictionary of Applied Chemistry Vol. 3, page 454. Referring to the attempts of Gossage, (1862) Gruneberg and Vorster (1876) and of Lieber (1878) states that the temperature required for the decomposition of salt is too high and the vessels employed cannot be made to last, and for these accounts the attempt had no practical results.

[3] U. S. Patent to Adolf Kayser dated Sept. 5th, 1901. Issued Sept. 9th, 1902.

The result of this slowness of action involved a too long heating of the briquetts, necessitating an abnormally large volume of nitrogen and fuel gases passing through the furnace to effect the result. The quantity of these inert gases was so great, that the hydrochloric acid fumes evolved, were not capable of efficient and practical condensation.

Adolf Kayser died in Lockport, N. Y., November 26th, 1910 of heart failure at the age of seventy-three. He came originally from the Hertz mountains, a simple yet energetic man in his habits, one loved by all and highly admired by those who could understand his clear philosophical reasoning. He, like Lablanc, failed to realize his thirty years dream of success. Unlike Lablanc, he was happy in his latter years in following his passion for original chemical research. He discovered a soluble sodic-silico-aluminate of high detergent value, now finding its way into commercial channels as a substitute for soap.

While he was thus employed as a chemist with The Electric Smelting & Aluminum Company of which the reader is President, I suggested that we make up some salt and clay briquetts adding charcoal or sawdust to the mixture to render them porous during heating; and test them out in a comparable manner with similar briquetts of clay and salt alone such as he had formerly used in his attempts to render the process mentioned commercial.

He did not think this mixture would work, as he was positive that it would destroy the oxidizing atmosphere needed in the operation to prevent the formation of valotile aluminum chloride (Al_2Cl_6). I believed that an oxidizing atmosphere was only necessary around the briquetts, and that it would gradually penetrate the mass of each briquette, and that a reducing atmosphere at interior portions of each briquette could not interfere with the desired re-action, as any aluminum chloride formed, would of necessity, change to oxide before leaving the briquette. Without mentioning this to Dr. Kayser, I insisted upon the trial being made. It was made. The bricks containing charcoal were converted into sodic-silico-aluminate in one-ninth the time that was required with like briquetts containing no charcoal. Seventeen degrees Beaume acid was condensed from a small apparatus in the face of imperfect control.

This experiment opened up an entirely new vista of success to the process. It meant that the volume of fuel gases and nitrogen necessary to pass through a charged furnace would become so reduced, as to permit of efficient commercial condensation of the hydrochloric acid evolved. It meant a great saving of fuel, and far greater capacity of output with the same cost of plant. The doctor and myself became equally enthusiastic. Our company acquired his patent for opening or rendering soluble the alumina in the form of sodic-aluminate from the sodic-silico-aluminate briquetts produced, and after two years or more of added experimental work in the laboratory, a large plant has been erected at Sewaren, N. J. The pictures from the lantern were taken before the plant was completed.

The process as a whole is easily understood. The clay, carbonaceous matter and salt are made into perforated briquetts, and after being dried in a drying kiln, they are passed on flat cars through a long furnace of the tunnel type which brings the briquetts to a temperature of about 1035°C.

Knowing the composition of the clay, and the percentage of salt in the mixture, steam is blown into the discharge end of the furnace over a train of cars covered with fire brick, with their iron parts sealed off, while through a vestibule at the other end of the furnace, loaded cars are gradually pushed forward by a hydraulic pusher whose speed is under control. The weight and composition of the material on the cars thus fed into the furnace is known, and the correct proportional weight of exhaust steam is passed into the furnace from the opposite end. From the charging end, the gases at a temperature too hot to attack iron, are sucked by a large blower and forced through a large hydrochloric acid condensing system. The temperature of the furnace is controlled by oil heat and measured by pyrometers. Most of the heat required is furnished by the carbonaceous material mixed with clay and salt of the briquetts. The re-action that takes place will vary according to the composition and mixture of the aluminous material and the salt, but typically, the final re-action is as follows:

$$\begin{aligned}Al_2O_3 2\,SiO_2+4\,NaCl+2\,H_2O+XH_2O+XC+XO= \\ (Na_2O)_2\,(SiO_2)_2\,Al_2O_3+4\,HCl+XH_2O+XXCO\end{aligned}$$

The surplus vapor of water, and the hydrochloric acid gas, are carried into the condensing apparatus and are condensed. The briquetts maintain their original form as the cars bearing them are gradually pushed out of the discharge end of the furnace, having been cooled by the inflowing rush of measured steam and a limited quantity of air.

The sodic-silico-aluminate briquetts formed have been made containing as high as 33% of sodic oxide. The above re-action would give 35.8% Na_2O. There is no appreciable loss of salt. While pure clays are preferred, all small amounts of iron pass off as iron chloride with the hydrochloric acid and are condensed with the first hydrochloric acid in the first condensers of a multiple series system. The acid produced is remarkably pure, free from arsenic, and but traces of sulphuric acid can come from iron pyrite if the same is in the clay. When briquetts are made containing 32% of sodic-oxide, the output of 30% hydrochloric acid should be about one-and-a-half tons of acid to one ton of salt and clay charged into the furnace.

The next step in this process is, to open the sodic-silico-aluminate, which is acid, to secure from it the sodic aluminate which it contains. This is accomplished by heating a mixture of ground acid salt with just sufficient lime to combine with the silica in it and form di-calcium silicate.

$(Na_2O)_2(SiO_2)_2\,Al_2O_3+4(CaO)=2(CaO)_2\,(SiO_2)+(Na_2O)_2Al_2O_3$

Limestone, calcite or marl in their chemical equivalent to lime may be used instead of anhydrous lime.

In the re-action just given above, any amount over two molecular weights of calcic oxide to each molecular weight of silica, leads to formation of insoluble calcic aluminate, and less than two molecular weights, is not sufficient and leaves undecomposed sodic-silico-aluminate. In each of these cases, marked loss in the recovery of alumina may occur. The mixture of lime and the acid salt is heated in a rotary cement furnace, or in a furnace of the tunnel type as above described, just to its clinkering temperature. After its discharge from the furnace, it is broken into fragments and these are in an excellent physical condition for effective leaching. Very nearly all of the sodic aluminate may be leached from this clinker, while there is left behind a white mass of dicalcium silicate containing some sodic aluminate.

Having secured the sodic aluminate in solution, the method of procuring the alumina and caustic soda therefrom is that already in universal use.

The residue of dicalcium silicate when heated in a cement furnace with one molecular weight more of lime gives a clinker that conforms in composition to Newbery's formula for the best and strongest hydraulic cement, but it has the advantage that all of the iron oxide has already been removed from the silica that goes into its composition, thus rendering it easy to secure a white cement by the use of limestone free from iron.

Such cement sells at about four times the market price of ordinary cement.

This process opens the way to secure the alumina cheaply, or as a by-product in conjunction with these other products, of great consumption in the industrial arts. There is required, 1.9 pounds of alumina, to produce one pound of aluminum by the present method of manufacture. This costs six and one half cents and is the heaviest item of cost in producing this metal. By the general introduction of this process, we may hope to see the cost of production of the metal aluminum reduced four or five cents a pound.

This process also furnishes a key to unlock the stores of potash from the world's mountainous masses of potash feldspar. As one way to do this effectively, the feldspar should be ground and mixed with either chloride of sodium or chloride of potassium and made with some clay and sawdust into the form of briquetts, then passed through a furnace under conditions similar to those described above. The solid product should then be submitted to Kayser's lime opening process. The clinker on leaching gives potassic aluminate or a mixture of this with sodic aluminate from which the alumina may be separated, and the salts of potash or potash and soda secured for use in fertilizers. The residue from leaching can then be converted into hydraulic cement.

A study of the re-actions herein given in connection with the volatilizing temperatures of the various chlorides of the common metals will throw much light upon the geological theories of formation of intrusive mineral veins.

Before closing this paper, I wish to express my pleasure at being able to do homage to Mr. Kayser and make known the splendid work of an able enthusiastic genial chemist, without whose aid the above described process as a whole, would never had attained the completeness that it now has, and the great usefulness that future years will confirm.

(Abstract)

ZEOLITES, NATURAL AND ARTIFICIAL

COMMERCIAL APPLICATION OF ARTIFICAL ZEOLITES

THOMAS R. DUGGAN
New York, N. Y.

In this paper it is shown that zeolites were known at an early date, and the part taken by them in vegetation, and the absolute lack of scientific investigation until quite a late date, when Dr. Gans, Professor of the Mining Academy of Berlin, examined many natural zeolites to determine their nature and the character of various interchanges they underwent in presence of various solutions.

The capacity of substituting bases varies considerably in the various minerals. Difference in behaviour in cases where the disparity in the percentage composition is not nearly so great led Gans to the assumption that the zeolites varied among themselves in constitution, and it was this variation which occasioned the difference in chemical properties. Gans ultimately succeeded in proving that there are two classes of zeolites. (Annual Reports of the Royal Prussian Geological Institute, 1905–6.)

These results illustrate the difference between the zeolites introduced by Ruempler into practice, and those introduced later by Gans.

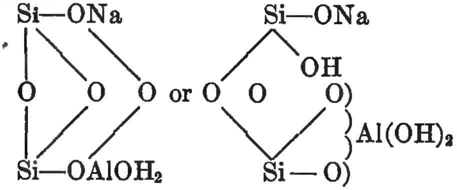
Gans has divided the zeolites containing aluminium into two classes:—

1. Zeolites which contain the alkaline earths and alkalies mostly combined with silicic acid, the bases of which can only be substituted in a very small proportion within a given time, and which he summarily described as "double silicates of aluminium." The alumina and the alkali and alkaline earth base

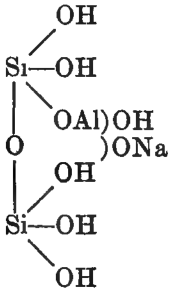
each substituted uniformly one hydrogen of the hydrate of silicic acid.

2. Zeolites which contain the alkaline earths and alkalies combined principally with alumina, and which substitute their bases nearly completely within a very short time. Gans called these "aluminate silicates," and are known commercially as "Permutit," as this description is best suited to describe their nature. The bases in these silicates are for the most part combined with the silicic acid by means of hydrate of alumina, one or two of the hydrogens of silicic acid being substituted by the group—Al(ONa), or less likely perhaps the group Al(ONa).
(OH)

Double silicate of alumina of the first group would be analcime, with the formula: $Na_2Al_2Si_4O_{12}+_2H_2O$, which could be expressed graphically thus:—



Chabasite belongs to the second class, with the formula: $Na_2Al_2Si_4O_{12}+_6H_2O$, which could be expressed graphically thus:—



Gans measured the absorptive power of the zeolites by digesting them two days with the above-mentioned Knop's solution of ammonium-chloride, and found that of the 129 mg. of the nitrogen contained in the solution there had been absorbed:—

By the	Apophyllite	00.0 mg.
"	Analcime	3.6 "
"	Natrolite	29.1 "
"	Zeolite Ruempler	30. "
"	Desmine	42. "
"	Stilbite	47. "
"	Chabasite	69. "
"	Artificial Zeolite of Gans	97. "

The above table shows that Ruempler's zeolites belong to the class of the aluminium double silicates owing to their inferior absorptive power.

Gans was the first who succeeded in manufacturing the so-called aluminate-silicates. He melted together three parts of kaolin, six parts of sand, and twelve parts of soda. The molecular composition of the resultant silicate is given by:

$$Al_2O_3+10SiO_2+10Na_2O.$$

The interesting part in the manufacture of Gans' artificial zeolites is that the method used is in accordance with nature's own methods.

The decaying process in nature takes its course according to no set rule, but in the artificial process, in Permutit manufacturing, the conditions must be carefully watched, and care has to be taken that the hydration does not go farther than the zeolite stage. This condition is the most difficult part in the manufacture of these substances. If carried on too far it would lead to decay, and if stopped too soon products of a felspar nature would be obtained. "Permutit" as named by Gans is derived from the Latin "Permutare"—to exchange.

The industrial uses of Permutit may be summarised thus:—

(1) Softening of water.
(2) Eliminating iron and manganese from water.
(3) Sterilising of water.
(4) Manufacturing of salts of a base by double exchange.
(5) Eliminating dangerous alkaline salts from the diffusion juice in the sugar industry.
(6) Obtaining gold from very dilute solutions, and many other exchanges which will readily occur to the chemist.

The most interesting property of Permutit is its power to exchange its own base by substitution of other bases. This process of interchange goes on extremely readily and follows closely the stoichiometric laws of chemistry.

The action of Permutit depends on its property of interchanging bases. Sodium Permutit has the formula $2SiO_2Al_2O_3Na_2O + {}_6H_2O$, and obviously its base is sodium. Now in hard water the bases are calcium and magnesium. If a water of given hardness is filtered through a bed of Sodium Permutit, the sodium in the Permutit is replaced by the calcium and magnesium of the water giving a Calcium-Magnesium-Permutit, while the acid radicles formerly united to the calcium in the water unite with the sodium.

The exchange takes place according to the following equations:

$$\begin{array}{llll} P\text{–}Na_2+ & (CaH_2(CO_3)_2 & =P\text{–}Ca+ & (2NaHCO_3 \\ & (CaSO_4 & & (Na_2SO_4 \end{array}$$

$$\begin{array}{llll} P\text{–}Na_2+ & (MgH_2(CO_3)_2 & =P\text{–}Mg+ & (2NaHCO_3 \\ & (MgSO_4 & & (Na_2SO_4 \end{array}$$

There will obviously come a time when all the sodium in the Permutit has been replaced by calcium and magnesium from the treated water. When this time arrives it is not necessary to recharge the filters with new Permutit, but the so-called "exhausted" Permutit can be readily "regenerated" or "revivified." This is done by the action of a solution of common salt on the exhausted Permutit. The laws of chemical exchange again come into play, the interchange being in this case in the opposite direction, sodium from the salt driving out the calcium from the Permutit.

Sodium Permutit can readily be converted into Ammonium Permutit, Tin Permutit, and Manganese Permutit.

If to Sodium Permutit a solution of ammonium chloride is added, Ammonium Permutit is formed, and a solution of sodium chloride.

$$P\text{–}Na_2+2NH_4Cl=P\text{–}(NH_4)_2+2NaCl.$$

This Permutit could be used in quantity to obtain valuable potash salts from waste waters according to the following equation; for example:—

$$P\text{-}(NH_4)_2+2KCl=P\text{-}K_2+2NH_4Cl.$$

The regeneration of this filter would be according to the equation:—

$$P-K_2+2NH_4Cl=P-(NH_4)_2+2KCl.$$

The characteristic property of Permutit in exchanging its own base against other bases has been made use of for the exchange of some metals, viz., manganese, iron, and tin.

The filtration of Manganese Permutit thus guarantees a water absolutely freed from iron and manganese, which cannot be done for industrial purposes by any other scientific method.

The same Manganese Permutit is used for clarifying water and for purifying it from germs.

During the filtration through the oxidised or reduced oxides of manganese without zeolites, or in conjunction with zeolites, however, the colloidal oxides of manganese are removed in the form of flakes with a high speed of filtration, and carry the suspended matter and germs of the water with them.

To put the whole purifying process into simple language, the germs are precipitated by forming a colloidal solution in the crude water by means of the Manganese Permutit, in which the germs are enveloped and are killed by regeneration of the Manganese Permutit with permanganate of potassium.

The properties of this product, its application in the process of water softening has been shown, and the reaction that takes place when water is to be freed from iron or manganese salts has been explained.

The sterilising action of this remarkable compound will probably be of equal importance in the course of time. There is here a wide field for further investigation, and it is more than probable that Permutit will find some application in quite new directions.

MOLEKÜLVERBINDUNGEN ALS PRIMÄRSTUFEN CHEMISCHER REAKTIONEN

C. Engler
Karlsruhe, Germany

In der Erklärung der ersten Vorgänge bei chemischen Reaktionen standen sich früher zwei prinzipiell von einander verschiedene Ansichten gegenüber: nach der einen findet, wenn zwei Moleküle aufeinander einwirken, von vornherein eine doppelte Umsetzung statt unter vorausgehender Dissoziation in die reagierenden Spaltstücke, nach der anderen lagern sich die reagierenden Moleküle primär zusammen und bilden Molekülverbindungen, die sich entweder intramolekular in die Endprodukte isomerisieren oder aber unter vorausgehender intramolekularer Umlagerung die sekundären Reaktionsprodukte abspalten.

Zweifellos findet in sehr zahlreichen eingehend studierten Fällen primär eine molekulare Anlagerung statt, und man geht wohl kaum fehl, wenn man für Reaktionen bei gewöhnlicher Temperatur auch häufig solche Additionsverbindungen als Primärprodukte da annimmt, wo sie nicht ohne weiteres in die Erscheinung treten. Auf der anderen Seite ist aber doch auch zuzugeben, dass, ganz abgesehen von der Ionenspaltung, bei vielen Reaktionen eine Dissoziation die Primärreaktion ist, bezw. sein muss, wofür als Beispiel nur die Ozonbildung durch elektrische Entladung und bei sehr hoher Temperatur angeführt sei, welche zweifellos die primäre Spaltung eines Sauerstoffmoleküls in 2 Atome zur Voraussetzung hat ($3O_2 \rightleftarrows 2O_2+O+O \rightleftarrows 2O_3$). Auch für viele andere Reaktionen ergibt sich ähnliches als Notwendigkeit aus dem Temperaturgleichgewicht anderen vor der eigenstichen Reaktion eintretenden Spaltungen.

Hier soll nur von der ersteren, den molekularen Anlagerung, die Rede sein, und zwar im weitesten Sinn. Einer der ersten in seinem Wesen bekannten Vorgänge dieser Art ist die Aldol-Reaktion nach *Wurtz* zu Additionsprodukten, welche unter Ausscheidung von Wasser zu ungesättigten Verbindungen kondensieren können; und auch schon *Kekulé* hat angenommen, dass allen Substitutionsreaktionen Additionsreaktionen vorausgehen.

Für die Oxydationsreaktionen habe ich gegenüber *van 'tHoff*, welcher auf Grund von theoretischen Erwägungen und von Versuchen von *Ewan* u. A. annahm, dass der Sauerstoff bei Autoxydationsvorgängen nur in ionisiertem, also atomistisch gespaltenem Zustand zur Wirkung komme, die Ansicht vertreten, dass sich der Sauerstoff dabei primär stets als ganzes Molekül an das zu oxydierende Molekül zu einem Moloxyd anlagere, worauf dann intramolekulare Umlagerungen oder hälftige oder vollständige Uebertragung des angelagerten Sauerstoffs an einen dritten Körper, den Acceptor, erfolgen könne. Dabei kann der primär wirkende Körper, der Inductor, auch selbst zum Acceptor werden. In ein neues, epochemachendes Stadium ist die Frage der additionellen Molekülverbindungen durch die Untersuchungen *Werners* über die Metalliake und analog konstituierte Metallverbindungen getreten, wobei unter Einfügung des Begriffs der koordinierten Systeme und unter Annahme von Neben valenzen wichtige Einblicke in den Mechanismus der Vorgänge bei der Bildung und Umsetzung von additionellen Molekülverbindungen genommen wurden. In genialem Ideengang hat es dann weiterhin *Werner* verstanden, seine theoretischen Ansichten für die Erklärung der optischen Aktivität und ganz besonders der *Walden'* schen Umkehrung zu fruktifizieren (an der Hand neuer von ihm konstruierter Modelle demonstriert der Vortragende sowohl die Umkehrung des Drehungsvermögens von Antipoden ineinander beziehungsweise in Racemate, als auch unter Annahme der Zwischenbildung additioneller Molekülverbindungen-den Mechanismus des Vorganges bei der *Walden'*schen Umkehrung[1] gemäss den *Werner'*schen Vorstellungen). Man erkennt dabei leicht, dass je nach dem Ort, an welchem das Molekül sich anlagert ein Rechts- oder ein Links- Antipode resultieren muss. Fast gleichzeitig und unabhängig von *Werner* ist auch *Emil Fischer* zu einer ganz ähnlichen Auffassung und Erklärung der *Walden'*schen Umkehrung gelangt, ebenso *Pfeiffer*, wenn auch auch *Biilmann*[1] nachweist, dass die an dem Modell des Ersterem[2] entwickelte Erklärung sich nicht vollständig mit der den tatsächlichen Vorgängen zugebenden Deutung deckt. Für sehr viele Fälle additioneller Primärreaktionen und deren Weiterverlauf bildet aber das *Fischer'*sche Modell ein aussgezeichnetes Demonstrationsmittel.

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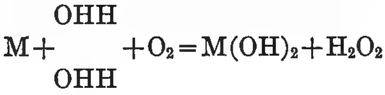
[1] Auf zwei senkrecht einander schneidenden Drahtringen schwingen, auf die letzteren aufgezogene, um das im Zentrum gedachte Kohlenstoffatom die 4 asymmetrischen Annexe in Gestalt von 4 verschieden gefärbten Kugeln, durch deren Verschiebung sich die gegenseitige Lage derselben (Konfiguration) nach Belieben in die eine oder die entgegengesetzte Spiegelbild—(enanthiomorphe) Modifikation verändern lässt.—Ein zweites Modell verdeutlicht die sterische Wirkung des Hinzutretens eines koordinierten Annexes nach der *Werner'*schen Vorstellung bei der *Walden'*schen Umkehrung. Die Modelle sind durch den Feinmechaniker Otto Behm in Karlsruhe i. B. zu beziehen.

Kehren wir jedoch zum Sauerstoff zurück. Auch dieser lagert sich primär als ganzes Molekül unter Bildung von Moloxyden oder Peroxyden an. Seitdem ich auf dem Internationalen Kongress für angewandte Chemie zu Berlin im Jahre 1903 über diese Autoxydationstheorie berichtet habe, sind nicht allein zahlreiche Bestätigungen derselben durch eine ganze Reihe von Experimentaluntersuchungen erfolgt, sondern man hat auch diese Vorstellungsweise des Sauerstofftransports auf das physiologische Gebiet, auf die Oxydationsvorgänge im lebenden Organismus übertragen. Auf diesem Gebiete ist besonders auch *Bach*, derfast gleichzeitig und unabhängig von mir die Peroxydtheorie aufstellte, erfolgreich tätig gewesen.

Schon viel früher hatte *Moritz Traube* die Ansicht aufgestellt und begründet, dass der Sauerstoff bei den Oxydationsprozessen stets als ganzes Molekül in Reaktion tritt. Er nahm dabei jedoch stets die Anwesenheit von Wasser an und die Zwischenbildung von Wasserstoffperoxyd nach dem bekannten Reaktionsschema:



$$M+\begin{matrix}\mathrm{OHH}\\ \\ \mathrm{OHH}\end{matrix}+O_2=M(OH)_2+H_2O_2$$

Bekanntlich giebt es noch viele Anhänger dieser Auffassung unter denen *Armstrong* eine führende Stellung einnimmt. Es würde aber zu weit ab von meinen eigentlichen Thema führen, wenn heute auch noch diese Frage zur Diskussion gestellt werden wollte. Nur das eine möchte ich bemerken, dass auch nach meinen Erfahrungen das Wasser, wenn oft auch nur in Spuren vorhanden, bei der Sauerstoffübertragung sehr oft eine ausschlaggebende Rolle spielt. So bildet sich nach eingehenden Versuchen, die ich gemeinschaftlich mit *W. Becker* anstellte,[1] entgegen dem Befunde *Boingaults*, aber in Uebereinstimmung mit theoretischen Ableitungen *Le Chateliers*, auch nach den Voraussetzungen der Peroxydtheorie, die den Anstoss zu unseren Versuchen gab, bei der Einwirkung von Sauerstoffgas auf Bariumoxyd bei völligem Ausschluss jeder Spur Feuchtigkeit selbst bei der günstigsten Temperatur von 500–600° keine Spur Bariumsuperoxyd, während es gelang unter Anwendung von Sauerstoffgas, welches im Liter nur 0,001 g Feuchtigkeit enthielt, bei derselben Temperatur 100-prozentiges Peroxyd darzustellen, ein Vorgang den wir durch die Gleichung interpretierten

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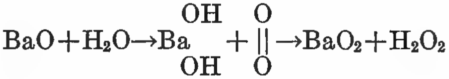
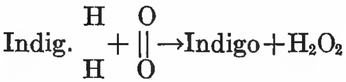
[1] Leib. Annal. *338*, 330.

[2] Ibid. *381*, 131.



$$BaO+H_2O\rightarrow Ba\begin{matrix}OH\\ OH\end{matrix}+\begin{matrix}O\\ \|\\ O\end{matrix}\rightarrow BaO_2+H_2O_2$$

Wegen der hohen Temperatur konnte zwar das Wasserstoffperoxyd nicht direkt nachgewiesen werden, man hat aber seine Bildung bei vielen analogen Reaktionen, die bei niedereren Temperaturen verlaufen, quantitativ feststellen können. So fand *Manchot* für die Autoxydation des Indigweise genau die der folgenden Reaktionsgleichung entsprechende Menge Wasserstoffperoxyd:



$$\text{Indig.}\begin{matrix}H\\ H\end{matrix}+\begin{matrix}O\\ \|\\ O\end{matrix}\rightarrow \text{Indigo}+H_2O_2$$

Jedenfalls tritt der Sauerstoff in zahlreichen Fällen bei Abwesenheit von Wasser nicht in Wirksamkeit.

Die Untersuchungen, welche in den letzten Jahren im Karlsruher Chemischen Laboratorium angestellt wurden, hatten zur Aufgabe, den Mechanismus zu studieren, nach welchem die molekulare Anlagerung des Sauerstoffs bei den Autoxydationsvorgängen ohne Mitwirkung von Wasser vor sich geht.

Nach früheren Versuchen von uns hatten sich die Fulvene zum

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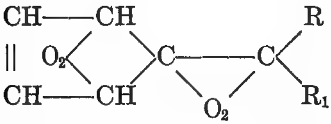
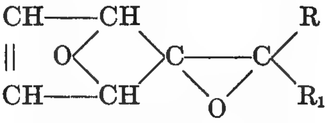
[1] Sitz. Ber. d. Heidelberger Akad. d. Wiss. *1910* 15. Abhandlg.

Studium dieser Frage als ganz besonders geeignet erwiesen. Von Dimethylfulven, Methyläthyl,—Methylphenylfulven werden stets je 2 Moleküle Sauerstoff unter Bildung von Di-Moloxyden (Di-Peroxyden) aufgenommen. Neuerdings wurden in Gemeinschaft mit *Schohl* auch die entsprechenden Di-Moloxyde des Fulvens selbst als eine sehr leicht zersetzliche, explosive Verbindung, ferner des Monomethyl-, Monäthyl-, Diäthyl-, Cinnamenyl- & des Methyl-Dimethylvinylfulvens (letzteres aus Cyklopentadien und Mesityloxyd) dargestellt. Sie entsprechen alle der folgenden allgemeinen Formel & gehen durch Abgabe von 2 Atomen Sauerstoff in die Monoxyde über, denen wahrscheinlich die entsprechende Konstitution zukommt:



Di-Moloxyde (Diperoxyde) der Fulvene



Di-Monoxyde der Fulvene

In beiden Fällen polymerisieren die primären monomolekularen Verbindungen rasch in hochpolymere Produkte.[1]

Für die obige Formel der Di-Peroxyde spricht 1.) bezüglich der Addition eines Mol. O_2 an die Seitenkette der von mir in Gemeinschaft mit *Dyckerhoff* gemachte Befund, dass das Cyklopentadien, dem diese Seitenkette bei sonst gleichen Formelgerippe fehlt, nur *ein* Mol O_2 addiert, während 2.) dem zweiten Sauerstoffmolekül die Stellung durch Eintritt in das konjugierte System des Cyklopentadienringes angewiesen ist.

Gelang es uns vorerst nicht, einen Anhaltspunkt dafür zu gewinnen, in welcher besonderen Art und Weise die Bindung der Sauerstoffmoleküle erfolgt, so konnte durch die im Karlsruher Laboratorium von *Staudinger* und seinen Mitarbeitern ausge-

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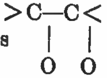
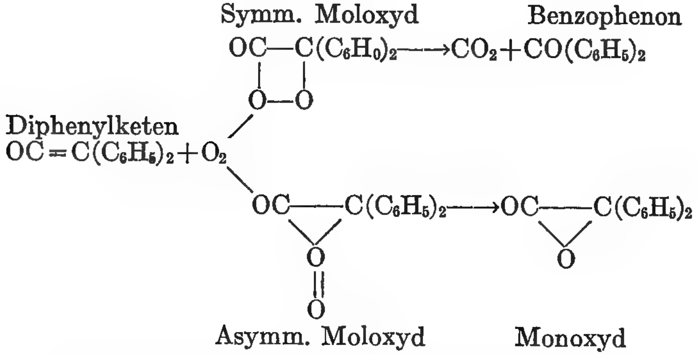
[1] Der Vollständigheit halber sei noch an die Möglichkeit des Zerfalls des Vierrings  $\begin{array}{c} >C-C< \\ |\quad\;| \\ O\quad O \end{array}$ in 2 O und einen ungesättigten Rest gedacht, wobei dann allerdings die andere Peroxydgruppe erhalten bliebe, was aber dem chem. Verhalten der "Dimonoxyde" nicht entsprechen würde.

führten schönen Untersuchungen über die durch Autoxydation gebildeten Peroxyde zahlreicher doppelsubstituierter Ketene (Ketoketene) auch einiges Licht auf die Konstitution der Fulvenperoxyde geworfen werden.

Nachdem er nachgewiesen hatte, dass im Allgemeinen das Sauerstoffmolekül sich besonders leicht an die Kohlenstoffdoppelbindungen nicht aber an ungesättigte Bindungen wie C=O, C=N, N=O, N=N addiert, dass aber auch in Bezug auf das Additionsvermögen durch die mit den ungesättigten Kohlenstoff verbundenen Atome und Atomgruppen grosse Unterschiede bedingt sind, gelang ihm noch der wichtige Nachweis, dass sich das Sauerstoffmolekül in manchen Fällen symmetrisch, in manchen Fällen unsymmetrisch an das doppeltgebundene Kohlenstoffpaar anlagert:



Aus der bekannten Tatsache leichter Spaltung der Vierringe ergiebt sich mit dem Nachweis der Bildung von Kohlensäure und Benzophenon des Diphenylketen-Peroxyds in der Wärme, dass das Sauerstoffmolekül symmetrisch angegliedert ist, während andererseits die Bildung des Monoxyds schon bei niederer Temperatur durch bloses Ausspringen eines Sauerstoffatoms aus dem Vierring sich nicht annehmen, dagegen aber ungezwungen dadurch erklären lässt, dass man von einem als beständig bekannten Dreiring, also von dem eben formulierten asymmetrischen Moloxyd ausgeht, dessen eines Sauerstoffatom leicht abspaltbar sein muss.

Versuche, welche *Schohl* auf meine Veranlassung ausführte, ergaben, dass alle Diperoxyde der Fulvene mit der Zeit von selbst, rascher bei vorsichtigem Erwärmen die Hälfte des aufgenommenen Sauerstoffs abgeben und dabei Produkte hinterlassen, die zwar nach ihren Eigenschaften als Polymerisationsprodukte aufgefasst werden müssen, denen aber durchweg die Elementarformel von Di-Monoxyden zukommt. Daraus muss geschlossen werden, dass der Sauerstoff in den Di-Peroxyden der Fulvene in asymmetrischer Form angelagert ist, oder dies doch bei der Bildung der Monoxyde war.

Nicht ohne Interesse ist es, dass der beim Erwärmen der Di-Peroxyde freiwerdende Sauerstoff, wie *Dyckerhoff* in meinem Laboratorium gefunden hat, Ozon-haltig ist; denn dieser Befund steht in Uebereinstimmung mit unserer Erklärung[1] der Bildung des Ozons aus Luftsauerstoff durch Berührung mit Phosphor, wobei die Bildung eines Peroxyds als Zwischen-reaktion ebenfalls angenommen wird, dessen sich abspaltende Sauerstoffatome sich mit molekularem Sauerstoff der Luft zu Ozon vereinigen. Man kann somit das Ozon auch als das Moloxyd eines Sauerstoffatoms bezeichnen.

Wenn bei derartigen Reaktionen des Zerfalls von symmetrischen Peroxyden unter Abgabe von Sauerstoffatomen scheinbar ein Widerspruch gegen Vorhergesagtes besteht, so muss demgegenüber doch auch daran gedacht werden, dass beim Zerfall einer beständigeren Verbindung manchmal als Zwischenbildung auch die unbeständigerere Form vor der Zersetzung angenommen werden muss, was der Grund sein mag, dass es bis jetzt nicht gelang bei der Zersetzung der Fulven-Peroxyde Keton-Abspaltung wie bei den symmetrischen Keten-Peroxyden wahrzunehmen. Die mit der Vierringspaltung konkurrierende Umwandlung in die labile Form, verläuft eben in diesem Falle rascher. Dafür, dass das Sauerstoffmolekül bei der Peroxydbildung sich primär in der labileren asymmetrischen Form anlagert, in der es sehr leicht 1 Atom Sauerstoff abgibt, also auch stark oxydierend wirkt, spricht auch der Befund, dass eine Lösung von

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[1] *Engler* und *Weipberg*, "Krit. Studien über die Vorgänge der Autoxydation" S. 61.

Dimethylfulven während man Sauerstoffgas hindurchleitet auf eine Indigolösung viel rascher bleichend wirkt, als wenn man fertiges reines Peroxyd mit der Indigolösung schüttelt. Für die primär labilere Bindung des Sauerstoffmoleküls bei Übertragung des Sauerstoffs an andere Stoffe gegenüber der Uebertragung durch die stabilere symmetrische Form spricht weiter der Versuch, welchen ich in Gemeinschaft mit *Steinkopf* in letzter Zeit ausgeführt habe.

Schüttelt man einerseits in Benzol gelöstes Baeyersches Benzoylhydroperoxyd in Kohlensäure atmosphäre mit Indigolösung, andererseits die entsprechende Menge Benzaldehyd, zu gleicher Verdünnung in Benzol gelöst wie das Benzoylhydroperoxyd in Sauerstoffatmosphäre mit Indigolösung, so tritt in letzteren Falle stets rascher Entfärbung ein, als im ersteren. Die Zeiten bis zur Entfärbung verhielten sich wie 6:5, bei teilweiser Sonnenbelichtung wie 8:5.

Durch diese Versuche erklärt die sich schon lange bekannte Tatsache, dass die meisten Sauerstoffüberträger, auch die "katalytisch" wirkende, den Sauerstoff energischer übertragen, wenn sie in Anwesenheit der zu oxydierenden Substanz mit Luft geschüttelt werden. Man darf annehmen, dass sich dabei primär stets zuerst das unbeständige asymmetrische Peroxyd bildet und das dies den Sauerstoff unter diesen Umständen an den Acceptor weitergeben kann, ehe seine Umwandlung in die beständige symmetrische Form erfolgen oder diselbe sich noch weitergehend umlagern kann. So wird Indigolösung mit Benzaldehyd, Terpentinöl, Phosphor oder Fulvenen, mit Luft oder reinem Sauerstoffgas geschüttelt, rascher entfärbt, als wenn man die vorher mit Sauerstoffgas geschüttelten Ueberträger (Benzaldehyd etc.) gleich oder nach einigem Stehen mit dem Acceptor (Indigolösung etc.) in Berührung bringt, wobei sehr oft, wie bei den meisten Katalysatoren überhaupt keine Wirkung mehr eintritt.

Als ein weiterer Beweis für die Richtigkeit dieser Auffassung ist es von Wichtigkeit, dass *Staudinger* in Gemeinschaft mit *Dyckerhoff* nachgewiesen hat,[1] dass die über das asymmetrische Peroxyd erfolgende Bildung des Diphenylketen-Monoxydes

[1] Dissertation *Dyckerhoff*, Karlsruhe S. 26.

hauptsächlich nur bei ganz niederer Temperatur (-80°) vor sich geht, während schon bei gewöhnlicher Temperatur und darüber die aus dem symmetrischen beständigeren Peroxyd abgespaltenen Produkte, Kohlensäure und Benzophenon, gebildet werden. Das sehr unbeständige asymmetrische Peroxyd ist eben nur bei ganz niederer Temperatur existenzfähig (und bildet dabei Monoxyd); schon bei gewöhnlicher Temperatur geht es in das beständigere symmetrische Peroxyd über und giebt dann die Spaltungsprodukte Kohlensäure und Benzophenon.

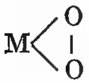
Will man nicht das Wasserstoffperoxyd als das asymmetrische Moloxyd des Wasserstoffs, also als $H_2=O=O$, und das Ozon als das asymmetrische Moloxyd eines Sauerstoffatoms: $O=O=O$ ansehen, für welche beiden Atomanordnungen aber die leichte Abspaltbarkeit je eines Atoms Sauerstoff aus Wasserstoffperoxyd und Ozon gegenüber den bisher meist üblichen Formulierungen spricht, so sind Peroxyde mit asymmetrischer Anlagerung des Sauerstoffmoleküls bis jetzt noch nicht isoliert worden, denn auch die in verdünnten Zustand einer Benzol-, oder Xylol-Lösung allem Anschein nach noch existenzfähigen asymmetrischen Peroxyde der Fulvene gehen beim Ausfällen aus diesen Lösungen mittelst Aether in die symmetrische Form über, indem sie gleichzeitig polymerisieren. Sie sind dann in Benzol bezw. Xylol (vorher löslich) nicht wieder löslich. Die für die Annahme einer Primärbildung asymmetrischer Moloxyde beigebrachten indirekten Beweise sind aber so wohlbegründet und experimentell so gut gestützt, dass über ihre Bildung als Primärstufe der Autoxydation kaum mehr ein Zweifel bestehen kann.

Nimmt man dazu, dass es auch noch Peroxyde und Oxyde giebt, wie z. B. Manganperoxyd, Bleiperoxyd, auch Kohlendioxyd, Silicium dioxyd Zinndioxyd u. s. w., in denen die beiden Sauerstoffatome völlig voneinander getrennt und je mit ihren beiden Valenzen gebunden sind, so hätte man ihrer Konstitution nach drei Arten von Sauerstoffbindungen zu unterscheiden, die gemäss der *Ostwald'* schen Stufenregel vom kleinsten Energieverlust bei Bildung verschieden möglicher Formen als primäre (I), sekundäre (II) u. tertiäre (III) Oxydationsphase aufzufassen wären und von I ab ansteigend unter Energieverlust unter entsprechender Zunahme ihrer Stabilität ineinander übergehen, also z. B.

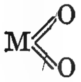
I (asymm.)

$M (H_2)=O=O$

II (symm.)



III



Moloxyde oder Peroxyde

Dioxyde

In den Moloxyden oder Peroxyden sind die beiden Sauerstoffatome noch direkt miteinander verbunden; in den Dioxyden nicht.

Geht man, was in neurer Zeit so oft geschieht, auf *Schönbein* zurück, so erkennt man in der Form II (u. I) seine *Antozonide* wieder, wozu er ausser dem Wasserstoffperoxyd das Bariumperoxyd, Strontiumperoxyd, Natrium-, Kelium-Peroxyd erst zählte, in der Form III aber seine *Ozonide* wie die Peroxyde des Bleis, Mangans-Nickels, Kobalts u. a. m.

Dass sich diese beiden Gruppen in Bezug auf ihre oxydierende Wirkung und Sauerstoffabgabe, auch im Uebrigen reaktiv (z. B. durch die Wasserstoffperoxydbildung der Antozonide) general von einander unterscheiden, hat ebenfallss chon *Schönbein* hervorgehoben.

REPORT OF THE VEREIN DEUTSCHER CHEMIKER WITH REGARD TO THE INTERNATIONAL REGULATION OF STANDARDS IN THE LITERATURE OF MINERAL ACIDS TO THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY IN NEW YORK

Dr. Neumann,
Wiesbaden

For some long time past the fact has made itself strongly,—not to say disagreeably,—felt amongst those interested in Mineral Acids, that writers of articles on this subject state their data in every conceivable way!

In writing of the manufacture of Sulphuric Acid some authors express the producing capacity or the output of a system in weight—units of chamber acids of 50 to 55°Bé; others express them in acids of 60 or of 66°Bé; yet a third part reckon by Monohydrate and finally,—particularly for the contact-systems,—data are found to be calculated on Anhydride.

If we add to the foregoing the data as to chamber-acid in degrees Twaddle instead of in degrees Beaumé, it will be perfectly clear, Gentlemen, that the want of unity is truly great! One can easily imagine that papers, lectures and discourses etc. of articles on this subject must frequently lose all enjoyment, auditors and readers being unable to reckon quickly and with ease the given deductions in the accustomed form. The great want therefore is for simple comprehensible international Standards,—and to determine these this International Congress is the most suitable occasion.

Although unity of weight would be most desirable in denominating all such data,—such as the Kilogramm, which speaks for itself, is accepted by all civilized nations with exception of the English and American,—we still would not venture to suggest the adoption of the Kilogramm for fear of hurting the national feelings of these two nations. On the same grounds we also refrained from proposing the use of the Metrical System as to standard measurement for chambers, towers etc. and the decimal (100 part) Thermometer to record the temperature.

If therefore, in consequence of this fear of wounding our cousins' patriotic feelings we cannot expect to be in the happy position of making an in every regard uniform International Agreement for the literature of Mineral Acids, we must content ourselves for the present with what can be accomplished without great difficulty. The first attainable step on the ladder of the International Agreement would be the determination of a standard for naming the strengths of acids.

For the Sulphuric Acid it seems advisable to give up all the old confusing records such as Acids of 52, 60, 66°Bé resp. 112, 142° etc. Twaddle and to appoint a regular standard, so that for the future the production, the output of a chamber-system, of a Glover, of a Contact-System would be expressible in Kos. (lbs.) Monohydrate of 100% or in Kos. (lbs.) Anhydride.

To which of these two,—whether Monohydrate or Anhydride,—the preference should be given, is not easy to decide. The manufacturers of Sulphuric Acid manufacturing by the Chamber System,—who are by far the most numerous,—will certainly be of the opinion that they would have conceded enough in having declared for the Monohydrate, which they have never even had the opportunity of seeing in their Works, much less of weighing or measuring it.

The other party, the Contact people, will be conceivably more radical, and one must acknowledge more logical, for they will hold that the standard Anhydride is and can be the only correct solution of this question. Their reason will be, that the calculation of an Oleum by Kos. (lbs.) Monohydrate would be an unnatural and unscientific step backwards, whilst for the Chamber Acid people it will be of no consequence, whether be chosen Monohydrate or Anhydride, both being not manufactured in the chamber. The necessity of a uniform regulation with regard to this question is urgent both for the chamber as well as for the contact system, if one takes into consideration the recent efforts of chamber people to successfully compete with the Contact Systems by concentrating the chamber acid to Monohydrate.

I must confess that we Germans did not perfectly agree on the practical profits of either SO_3 or H_2SO_4, and we should like to leave it to the Congress to decide, which of these two would make the most suitable standard. To whichever of the two the preference be given, the choice will prove agreeable to us, for it will,—once and for all,—make an end to the really wretched confusion on this field.

In the case of this first part of our motion being accepted, it must logically follow that in the future must be expressed the consumption of a Chamber System of Nitric Acid of 100%, —(instead of those of 36 or 40°Bé resp. of 66,5 or 76°Tw.),— referred to 100 Kos. (lbs.) of made Sulphuric Monohydrate or Anhydride in place of 100 Kos. (lbs.) Sulphuric Acid of 52, 60°Bé resp. of 113, 142°Tw. or even of 100 Kos. (lbs.) of burnt Brimstone, pyrites or Laming's gas purifying mass. You will observe, Gentlemen, that also in this regard the confusion is considerable owing to the many existing and really used variations.

Further, with reference to the manufacture of Nitric Acid it must be intelligible that for the future all data would be expressed by the Nitric Acid Monohydrate and not as formerly by Nitric Acids of 36, 40, 44, 47°Bé resp. of 66,5, 76, 88°Tw. and by such of 97, 98, 99%.

Regarding the manufacture of Muriatic Acid it seems to be logical to continue in an analogous way and to say for instance x Kos. (lbs.) HCl of 100% in the form of a Muriatic Acid of 16, 20, 22, 23°Bé or 25, 32, 36, 38°Tw.

However I have not been commissioned by the Verein Deutscher Chemiker to make this last proposal, for they have not yet decided to take up a standpoint on this question in consideration of the existing difficulty of accustoming the Muriatic Acid specialists and manufacturers to a rapid comprehension of the unaccustomed notion of Chlorhydric Acid Monohydrate.

In order to avoid any possible misunderstanding I should just like to impress on you the fact, that we do not intend with our proposals the slightest encroachment on the inner management of the factories. What we in reality desire is only the most uniform possible standard in regulation of the relative records in the literature and statistics of the Mineral Acid Industry.

It goes without saying that even a decision of this International Congress would not oblige anyone to use the proposed standards. However we think that the influence of the editors of periodicals on applied chemistry would suffice to induce narrow-minded authors to submit to the new resolutions in order to make their compositions better understood. We therefore suggest, that the eventually accepted resolutions should be brought to the notice of the said editors at the earliest possible moment by the Literary Committee of this Congress.

In conclusion may I be allowed to state concisely our proposals.

I. In the literature, statistics etc. of the Sulphuric Acid for the recording of the producing strengths, capacities, etc. the named quantities of Sulphuric Acid are to be expressed by either kos. (lbs.) Monohydrate or by Kos. (lbs.) Anhydride.

In the chamber system the consumption of Nitric Acid is to be expressed by percents of its Monohydrate with reference to 100 Kos. (lbs.) of made Sulphuric Acid Monohydrate resp. Anhydride.

II. In the same way in the manufacture of Nitric Acid its quantity to be named is to be expressed by Kos. (lbs.) of its Monohydrate.

III. In analogous way in the manufacture of Muriatic Acid its quantity to be named might be expressed by Kos.(lbs.) HCl in the form of any contained acid of say 20°Bé (32°Tw.).

ON THE METHOD OF PRODUCING BICALCIC PHOSPHATE WITH THE HELP OF ELECTROLYTICALLY PRODUCED ACID AND ALKALI

PROF. W. PALMAER

In order to meet the ever growing demand of agriculture for phosphate fertilizers, the following, as we know, are the chief preparations at present produced:

acid phosphate
basic slag
bone meal
bicalcic phosphate

which are here given in the order corresponding to the amount produced, acid phosphate being the phosphate fertilizer most largely produced, the annual output amounting to circa 10,000,000 tons.

Bicalcic phosphate has been produced hitherto only in small quantities, the production in Germany and France, for instance, during 1900, amounting to about 5,000 tons for each country. Hitherto this product has only been obtained as a by-product in the manufacture of glue, i.e. in the process when bone is soaked in diluted hydrochloric acid, whereby the main product in the manufacture, the glue substance, remains undissolved, while a solution of bone phosphate is obtained as a by-product. This is turned to account by precipitation with lime, by which means bicalcic phosphate is obtained.

On the other hand it is a long while ago since it was first proposed to obtain bicalcic phosphate as the chief product from every kind of raw phosphate in the same way, viz. by extracting the raw phosphate with hydrochloric acid and precipitating the solution thus obtained with lime. This method would have the advantage that one could make use of very poor and otherwise valueless raw phosphate, provided it does not contain too large a proportion of any useless, soluble compound, such as carbonate of lime. In the production of acid phosphate, on the other hand, one can not utilize raw phosphate with a lower percentage than circa 50% bone phosphate, since owing to the admixture of gypsum the percentage in the acid phosphate of available phosphoric acid is only about half that of the raw phosphate's percentage of phosphoric acid, and consequently consideration of freight charges for the prepared article excludes the use of a raw material in which the percentage is low.

However, it has hitherto shown itself that the price of hydrochloric acid has been too high for the adoption of this method. This in its turn is due to the fact that the production of hydrochloric acid according to the old methods entailed the sacrifice of sulphuric acid.

But the case is different if the acid is produced in such a way that a suitable salt, for instance perchlorate of sodium, is eletrolyzed with a diaphragm, so that free acid is generated in the anode chamber, and a solution of caustic alkali in the cathode chamber. With an electrolyzing tension of 4½ volts and 80% current efficiency it is easy to calculate that in order to produce the kilogram equivalent of acid 182 horse-power hours are required, whereby the alkali necessary for the precipitation of the bicalcic phosphate is obtained at the same time without additional cost in the cathode chamber. If we assume that 1 electric horsepower can be obtained for $10 a year—the usual price in many parts of Europe and presumably in many places in America—then the cost of the equivalent of 1 kilogram of acid amounts to circa 24 cents, the alkali being obtained at the same time; while with the old method lime had to be purchased. There is no outlay for material beyond what is caused by spilling &c., as the electrolyte regenerates, as will be seen from what follows.

If we assume that the price of 1 ton of chamber acid with 65% H_2SO_4 is $5, we shall find that the cost of the equivalent of a Kilogram of H_2SO_4 (49 Kg.) is circa 38 cents.

This calculation consequently shows that provided the remaining outlay for the electrolytic process can be kept within reasonable limits, it should be assured of success, especially as it allows of the utilization of otherwise valueless raw phosphate or refuse.

This calculation was the basis of my investigations, the object of which was consequently to try and make the method economically feasible, chiefly by finding a suitable electrolyte, and by constructing a serviceable electrolyzer.

As in the process there is no consumption of chemicals, beyond loss by spilling, &c., the cost of the sulphuric acid used in producing acid phosphate is replaced by the cost of the electric power. The economic result of the method depends therefore in the first place on the price of the power.

Before proceeding to enter upon detailed descriptions, it will be advisable to give a general survey of the method.

I. GENERAL FEATURES OF THE METHOD

In an apparatus expressly adopted for the method, a solution of chlorate or perchlorate of sodium is electrolyzed. In the anode chamber an acid is thereby generated—chloric or perchloric acid—and in the cathode chamber a solution of caustic soda. The electrolysis is continued until a certain quantity of the dissolved salt has been separated into acid and alkali. The anode and the cathode solutions are led off into separate receivers. The acid anode solution is then allowed to work in a dissolving battery upon raw phosphate, in which process the phosphate is dissolved. Into the solution thus obtained the alkaline cathode solution is introduced, the whole being meanwhile kept vigorously stirred, until the liquid bears evidence of a slightly acid reaction; to obtain that result about half the cathode solution is required. In the process bicalcic phosphate is precipitated as a finely crystalline precipitation, which is drained off by filtration and washed. The filtrate, which contains $\frac{1}{3}$ of the lime originally dissolved, but hardly any phosphoric acid, now has added to it the remainder of the cathode solution, which has previously been saturated with carbonic acid from fuel-gas. The lime is precipitated as carbonate, which is allowed to settle. The solution remaining above it is then drawn off. The original electrolyte is regenerated by its means and again enters the electrolyzing apparatus.

II. THE NATURE OF THE ELECTROLYTE

With reference to the electrolyte, the salt used should be of such a nature that its acid may yield, in conjunction with lime, an easily soluble salt, and of a kind which is not subject to change during electrolysis.

As electrolytes, solutions of perchlorate of sodium or chlorate of sodium are suitable, or else mixtures of those salts, the presence in small quantities of other salts, for instance chlorides, being of no account. Both these salts can now, since they have been produced by electrolysis, be had at reasonable prices.

Perchlorate of sodium is an ideal electrolyte for the purpose in question. On electrolyzing its solution with a diaphragm, sodium hydrate is formed in the cathode chamber and perchloric acid in the anode chamber, while hydrogen is developed at the cathode and ozonic oxygen at the anode. No noticeable reduction of the salt occurs at the cathode, nor any other change, and the solution of perchloric acid obtained is perfectly constant at such temperatures as can be taken into consideration in the electrolyzing (maximum 50°C.). Furthermore, the salt is exceedingly easily soluble (deliquescent) and thus easy to wash away.

Chlorate of sodium is less constant, in that the chloric acid solution formed in the anode chamber already begins to decompose at 40°C., free chlorine being developed. Moreover, it is considerably reduced at the cathode to chloride. But the principal change is that the development of oxygen at the anode almost ceases, because the chlorate there is oxidized to perchlorate. For this reason a start can very well be made with chlorate of sodium, since though the drawbacks mentioned (the decomposing of the chloric acid and the reduction of chlorate) appear at first, they soon disappear, viz., when the chlorate has become perchlorate of sodium. Even if you begin with chlorate of sodium, the electrolyte consists after a while of pure perchlorate, which, as has been said, suffers no further change.

The loss of perchlorate of sodium by spilling and incomplete washing need not, according to our experience, be estimated higher then at about 1% of the weight of the bicalcic phosphate developed.

Another way of carrying out the process is this:—A solution of chloride of sodium is electrolyzed so that a solution of caustic soda and free chlorine is obtained. The chlorine is transformed in the usual way into hydrochloric acid wherewith the raw phosphate is dissolved, whereupon a precipitate is formed with this caustic soda. The salt is then regenerated as before. Although common salt is cheaper than perchlorate of sodium or chlorate of sodium, the process by several reasons (depreciation of anodes, losses of chlorine, etc.,) is not so advantageous.

However, both the processes here described are protected by patent rights.

III. THE ELECTROLYSIS

The electrolysis of the perchlorate of sodium solution must be carried out, as has been mentioned, in a diaphragm apparatus, and it is clear that the problem is to find a suitable anode and a suitable diaphragm. Both difficulties have been solved in a perfectly satisfactory manner, but for the present I can not enter into details.

The voltage has been found to amount on the average to 4.5 volts per cell, including loss in connections. Of course it varies somewhat, according as the diaphragms are newly inserted or not, the electric contacts recently overlooked or not, and with the temperature of the solutions, which may vary at different times of the year; but, as stated, the average voltage is 4.5. The polarisation amounts to 2.97 volts.

In a diaphragm process, where the new substances formed at the cathode and the anode remain in the solution (in this case alkali, or perchloric acid), the current efficiency continually diminishes, of course, in proportion as the newly formed substances begin to take part in the current circuit. We generally produce solutions with 1 gram equivalent of acid or alkali per liter, and have then a current efficiency of 82% and a ballast of undercomposed salt in both acid and alkali solutions.

IV. THE RAW MATERIAL AND ITS UTILIZATION

Of course the high-percentage raw phosphates used to make acid phosphate can be employed for the process, but it is not for such, but rather for low-percentage raw phosphates, at present worthless or of inferior value, that the process is primarily designed. Here I need only mention in illustration low-percentage apatites and apatite waste, waste from magnetic separation of phosphoric iron-ore, and certain low-percentage phosphorites.

As the process consists in dissolving the bone phosphate occurring in raw phosphate, and then precipitating bicalcic phosphate from the solution, the product obtained will always be of the same nature, irrespective of the percentage of the raw phosphate. We have employed raw products whose percentage of bone phosphate varied between 20% and 88%.

Furthermore the raw phosphate need not be finely pulverised, provided that the bone phosphate is not embedded in insoluble minerals and that other soluble substances, such as certain silicates, do not occur in too great a quantity;—we have worked with material of as coarse crushing as 5 cm.

Assuming that the solution of bone phosphate is effected according to the formula $Ca_3P_2O_8+6HC10_4=3Ca(C10_4)_2+2H_3PO_4$ then per liter of 1-normal acid 23.7 grams of phosphoric acid should be dissolved. It can be foreseen, however, that the reaction, in contrast, for instance, to the reaction $CaCO_3+2HClO_4=Ca(ClO_4)_2+H_2O+CO_2$ will not proceed quantitatively, since phosphoric acid is a much stronger acid than carbon anhydride. We have also found that we must reckon with a somewhat lower figure, say 20 gr. P_2O_5 or 43.6 gr. $Ca_3P_2O_8$ per liter of 1-normal acid. This figure holds good provided that no other bodies soluble in acids occur in the raw phosphate.

Of such, in the first place, we must take into consideration calcium carbonate, for, as we know, it readily and completely dissolves in acids. As the equivalent weight for phosphoric acid (P_2O_5) is 23.7, and for carbon anhydride (CO_2) 22, we can consequently state that 1% of CO_2 in the raw phosphate causes approximately the same consumption of acid (or of energy) as 1% of P_2O_5, without giving any product of any value to speak of (the amount of carbonate of lime obtained as a by-product will of course be correspondingly greater). A raw phosphate which contains 20% of P_2O_5 (as $Ca_3P_2O_8$) and 2% of CO_2 (as $CaCO_3$) consequently requires about 10% more energy than a raw phosphate with the same proportion of phosphoric acid, but free from carbonate of lime.

Iron oxides (iron-ores), on the other hand, are only dissolved very slightly. We found that after 24 hours' shaking at the usual temperature with 1-normal acid, there was dissolved
of magnetite a quantity corresponding to 0.24 grs. Fe_2O_3 per liter
" hematite " " " " 0.20 " " " "
which amounts are of no practical importance.

Most silicates are, as we know, insoluble in diluted acids. However, silicates may occur, e.g. together with apatite, which are easily soluble that they dissolve to a noticeable degree if the acid is in contact with them for any length of time after most of the phosphate is dissolved. Attention must be paid to this in the course of the lixiviation, and the work regulated accordingly.

As regards the utilization of the bone phosphate in the raw material, we can as a rule count upon extracting 98% of it, sometimes more, sometimes a little less, viz., when easily soluble silicate is present.

V. PRECIPITATION OF THE BICALCIC PHOSPHATE AND CALCIUM CARBONATE

To precipitate the bicalcic phosphate we made use, as before stated, of the solution of caustic soda obtained by electrolysis, which is introduced into the phosphate solution by means of a sprayer.

The employment of the soda solution as a precipitator, instead of lime-white, has a considerable advantage. For the fact is that as soon as the solution has become alkaline at any point, bone phosphate is precipitated there instead of bicalcic phosphate. This once precipitated bone phosphate is only slowly converted into bicalcic phosphate, even if the average acidity of the liquid is such that only bicalcic phosphate ought to occur. At least a portion of the bone phosphate thus formed remains therefore in the precipitated bicalcic phosphate. The bone phosphate thus precipitated is very finely distributed, it is true, and is even soluble after drying in 2% citric acid; but it has no manuring value worth speaking of. The phosphoric acid precipitated as bone phosphate, must therefore be looked upon as lost.

Now it is clear that it would be much easier to avoid the formation of bone phosphate if a sodium hydrate solution, distributed in jets, were employed as the precipitator, than if lime-white were used, since in the latter case we get particles of solid calcic hydrate, round which the solution easily becomes alkaline.

Experience also proves that in employing sodium hydrate, which is added until the phosphate solution is still very slightly acid or only just neutral, bicalcic phosphate can be precipitated so completely that only 0.1 to 0.2% of all the phosphoric acid remains unprecipitated, while 98% of the phosphoric acid in the bicalcic phosphate is soluble in citrate, and thus only 2% of the phosphoric acid is present as bone phosphate.

The precipitated bicalcic phosphate, which is microcrystalline, is filtered off, washed and dried. It thus forms a light, pure white powder, and its proportion of citrate-soluble phosphoric acid amounts to from 35–38%, according to the completeness of the drying.

If we call to mind that about 2 % of the phosphoric acid in the raw phosphate is left behind in the extraction, that no quantity to speak of remains unprecipitated, and that about 2 % is recovered as precipitated bone phosphate, we shall find that about 96 % of all the phosphoric acid in the raw phosphate is extracted in the process as valuable citrate-soluble phosphoric acid.

The bicalcic phosphate obtained shows, even if it contains iron and aluminum phosphate, no retrogradation of soluble phosphoric acid, which is simply due to the fact that it can be perfectly dried, after which no conversion can take place. On the other hand, as we know, retrogradation shows itself in damp acid phosphate. The following analyses may be quoted to show that retrogradation does not occur:

	Total P_2O_5 %	Citrate-soluble P_2O_5 %	Citrate-soluble P_2O_5 in % of total P_2O_5
fresh	35.45	34.58	97.54
after 3 months	36.02	35.13	97.53
" 6 "	36.54	35.72	97.75

From the filtrate of the bicalcic phosphate is precipitated, as we have already mentioned, the lime that remains in the solution, together with the rest of the sodium hydrate solution, after the latter has been saturated with carbon anhydrid from fuel gases, as carbonate of lime, which can be used as a fertilizer or in chemical workshops.

Its mass corresponds to about $\frac{1}{4}$ of the weight of the bicalcic phosphate obtained, if the raw product used be free of carbonate. If calcium carbonate occurs in the raw product, the mass obtained in the process will be proportionately increased.

VI. POWER EXPENDITURE

From the statements given above, it is easy to calculate what electric horse-power (direct current) produces per year of 350 × 24 = 8400 hours; it will work out at 2.24 tons of bicalcic phosphate with 35% of citrate-soluble phosphoric acid, if free of carbonate. If a 38% article is produced, $\frac{2.24\times35}{38} = 2.06$ metric tons per horse-power year will be obtained, etc. The production with carbonaceous raw product has been stated above.

VII. VALUE OF BICALCIC PHOSPHATE FERTILIZER

Careful experiments extending over many years have been made, partly by Professor *H. G. Söderbaum*, Agricultural Chemist at the Central Institution for Experimental Agriculture, Stockholm, partly by Dr. *Hj. von Feilitzen*, Director of the Swedish Peat Society, Jönköping, Sweden. Professor Söderbaum's earlier investigations are reported in "The experiment Station Record," edited by the U. S. Department of Agriculture, Washington, Vol. XIV., No. 10, pp. 951–2 (1903), and he has also summed up the result of his investigations under the title of "Vegetationsversuche mit gefälltem Calcium-phosphat" in the "Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich," 1908, pp. 506–510. Dr. von Feilitzen has communicated the chief results of his investigations in the "Journal für Landwirtschaft," 1910, pp. 33–43.

As Dr. von Feilitzen is going to give an account of his further investigations at the Congress, I will here only briefly mention the chief result of his and Professor Söderbaum's culture trials.

The result of the experiments in cultivation is, that the citrate-soluble phosphoric acid in the bicalcic phosphate proves to possess the same fertilizing value as the water-soluble phosphoric acid in the super-phosphate, and consequently the same value as a trade product. That result might, indeed, have been foreseen, inasmuch as it is probable that the superphosphate in the soil is rapidly transformed into bicalcic phosphate through the agency of the compounds of lime present there. This result is supported by the trials carried out by practical agriculturalists, who are well satisfied with both the result of the phosphate and its qualities in general. Owing to its high percentage the freight-charges are low for the valuable ingredient, and a very small amount need be manipulated by the farmer. It is in all other respects easy to handle and does not damage the sacks in the least.

VIII. THE SUPERIOR ADVANTAGES OF THE ELECTROLYTIC METHOD

The merits of the electrolytic method are as follows:—

(a) It admits of the use of cheap low-percentage raw phosphate, not available for the superphosphate industry.

(b) By it, a phosphate containing 35—38% of soluble phosphoric acid is obtained, even from low-percentage raw material.

(c) Freightage for a given quantity of phosphoric acid in the finished article is only about half that in the case of ordinary superphosphate.

(d) Retrogradation of soluble phosphoric acid when stored does not occur.

(e) The raw phosphate need not be reduced to a finely powdered state.

(f) Bicalcic phosphate can be employed as a fertilizer on all kinds of soil, even on sandy and boggy land.

(g) Bicalcic phosphate will be of excellent use in the manufacture of "complete fertilizers."

(h) Sacks are in no wise damaged by the product.

(i) The product is a finely divided, white powder, which is easily spread on the field.

The process is now being carried out in a small factory, the first factory, belonging to the Difosfat Company, Trollhättan, Sweden.

THE ANHYDROUS CONDITION AND STABILITY OF FUSED LITHIUM PERCHLORATE, AND THEIR BEARING UPON THE ATOMIC WEIGHT OF SILVER[1]

Theodore W. Richards and Marshall W. Cox
Harvard University, Cambridge, Mass.

In a comprehensive research upon the atomic weights of lithium and silver, H. H. Willard and one of the present authors[2] devised and perfected an entirely new method for determining the latter of the two atomic weights. This method involved the treatment of pure anhydrous lithium chloride with excess of perchloric acid, and the drying of the lithium perchlorate thus formed for a long time at a temperature of about 300°. From the weights of factor and product, together with the ratio of lithium chloride to silver (determined at the same time in another series of analyses made in the usual way), it is easy to calculate the atomic weight of silver with reference to that of oxygen in the following fashion, assuming that four times the atomic weight of oxygen is 64,000:—

$$\frac{Ag}{64.000} = \left(\frac{LiCl}{LiClO_4 - LiCl}\right)\frac{Ag}{LiCl}$$

The value of the outcome depends entirely, as usual, upon the purity of the three solid substances concerned. Silver is capable of being made nowadays in a state of great purity. Lithium chloride also can be prepared in a state very free from contamination, even with water, by methods elaborated at Harvard; but lithium perchlorate, which has been less studied, cannot be heated to a red heat without decomposition, and its freedom from volatile impurities is less certain. This fact was fully appreciated by the experimenters, and they promised to investigate further the question concerning the purity of the lithium perchlorate. Obviously any water retained by this salt would decrease the apparent atomic weight of silver, by increasing the denominator of the fraction within the parenthesis. On the other hand, any trace of decomposition suffered by the salt would have the opposite effect. The resulting contamination of the perchlorate by chloride or chlorate is easy to detect; but the retention of minute traces of water is much more difficult to discover. The present investigation, which has been greatly prolonged because of the subtle nature of the problem, has primarily to do with the question as to the anhydrous condition of the lithium perchlorate, and we take pleasure in stating that the question, if not wholly settled, has now at least been carried much further than before. The evidence now available points towards the improbability of the retention of weighable amounts of water by lithium perchlorate at 300°. It is true that this result was not wholly unexpected, for the salt came to satisfactory constancy in weight, even at 280°, and a rise of 30° had no effect upon this weight. Moreover, one of us in collaboration with G. S. Forbes,[1] showed some time since that silver nitrate, a salt nearly as soluble as lithium perchlorate, retained practically no water at all at a much lower temperature, namely, 200°. Nevertheless, the outcome is satisfactory, and leads one to believe that the method under discussion for determining the atomic weight of silver is one of the very best.

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[1] The authors are much indebted to the Carnegie Institution of Washington for funds needed for the elaborate apparatus employed in this research.

[2] Richards and Willard, Pub. Carnegie Inst. of Washington, No. 125.

The determination of the possible traces of water held by fused lithium perchlorate, which had been heated to constant weight at 300°, involved three main steps. In the first place, a series of experiments was carried out, in each of which about 12 grams of the salt thus dried were heated to 400° for some time, while the quartz flask containing the fused salt, was swept out with pure dry air. This air was afterwards passed through a heated tube containing silver wire and a weighed tube of phosphoric oxide; the latter would catch and determine the water expelled. Even at this higher temperature the decomposition of the perchlorate was very slight. Then two further experiments were made with the temperature of the perchlorate raised to 430°, where the salt decomposed easily; and the evolution of the oxygen was continued until more than half of the salt was converted into lithium chloride. Finally, controlling experiments were carried out in which everything was maintained in precisely the same condition except that no perchlorate was present at all; and these blank trials served to evaluate the necessary errors of experimentation with the complicated apparatus. The crucial points of the whole problem were found to lie, first, in thoroughly sweeping out the whole apparatus with perfectly dry air for many hours before beginning the experiment; and, secondly, in filtering the pure air, both before it entered the flask containing the perchlorate, and also before it entered the weighed drying tube. The filtration was necessary in the first case to remove the finest particles of dust which are only very inadequately held by the usual forms of purifying towers, and in the second case to hold the impalpable powder of lithium salt carried off by the bubbles of gas escaping from the fused mass. In each case the gas-filter consisted of a fine grained porous cup, suitably cemented within the glass apparatus; and the second gas-filter was heated during the experiment so that the lithium salt held there should not retain any of the water possibly expelled from the fused salt.

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[1] Richards and Forbes Carnegie Institution of Washington, Publication 69, p. 47 (1907)

The outcome was as follows:—three experiments, in which salt previously dried at 300° was further heated at 400°, showed gains in the pentoxide tube, amounting respectively to 0.00020, 0.00027, and 0.00029, in average 0.00025 gram. Two similar experiments, in which the temperature was raised to 430°, showed corresponding gains in the pentoxide tube, amounting respectively to 0.00026 and 0.00039, in average 0.00033. Finally, two "blank" experiments, in which no lithium perchlorate was present at all, showed gains amounting respectively to 0.00028 and 0.00034, in average 0.00031 gram.

In short, neither of the series in which lithium perchlorate was present deviated more from the control-experiments than an account which might be due to the necessary errors of experiment. Clearly, lithium perchlorate previously dried at 300°

cannot be made to evolve as much as one part in a hundred thousand of its weight of water by very drastic treatment.

At first sight this result seems to be conclusive; one might be inclined, without further thought, to maintain that lithium perchlorate thus dried is truly anhydrous; but the problem is not as simple as it appears. The fact that the salt *gives off* no water on decomposition does not necessarily prove that traces of water are not held as lithium hydroxide at the moment of decomposition; for lithium hydroxide would not yield up its combined water by mere heating at a temperature even far above 430°. Nevertheless, a possible saving agency appears in this case in the material of the walls of the flask, which is greatly attacked as the salt decomposes. It is conceivable that any lithium hydroxide present would combine with the silica; and the water which might otherwise be held may thus be set free. For once the containing vessel, which so often introduces disturbing impurities, may actually aid the experimenter by its lack of resistance to the reagents which it holds.

Reassuring as this hypothesis may be, it has nevertheless not yet been proved; and one is not justified in considering the problem as wholly solved. A known amount of lithium hydroxide must be added to fused dry perchlorate, in order to discover if the mixture can be made to disengage its firmly imprisoned water by heating to 400° in contact with silica. This additional question will be tested experimentally in the near future. The mere heating of the perchlorate seems to have been carried as far in the present work as is worth while. The whole matter is a striking example of the subtlety and difficulty of a problem which might appear at first sight to be exceedingly simple.

The stability of lithium perchlorate evidently plays an important role in this performance. This stability was apparently affected in a very interesting way by the air-filter which removed the dust from the air passed over the salt. Without the dust-trap interposed in the air current, the salt bubbled in lively fashion at 350°; with it, the temperature could be kept for an hour and a half even at 400° without visible evolution of gas. The loss of weight in the latter case amounted to only a few hundredths of a percent. Thus there seems to be some very finely divided matter in ordinary air—perhaps organic dust of almost submicroscopic fineness—which catalyzes the decomposition of lithium perchlorate by heat. This is an important fact in relation to the stability of the salt, as well as in its bearing on other similar cases.

In a few words the contents of this paper may be summarized as follows:

Lithium perchlorate fused at 300° was found to lose no appreciable trace of water when gradually heated to 400° without much evolution of oxygen, or when quickly heated to 430° with far-reaching decomposition. Thus the salt used by Richards and Willard in their work on the atomic weight of lithium and silver appears to have been in this respect as pure as it could possibly be made. The present work therefore adds support to the value for silver 107.871, as found in the former work. Nevertheless, although as far as it goes the new work confirms the old, no one is yet in a position to state absolutely that a trace of water is not held by the residue left after the decomposition of the salt. This matter will be tested yet further in the future by methods already indicated; the question is of consequence, because it touches vitally one of the most important of all the atomic weights.

UEBER DIE ZUSTANDSDIAGRAMME DES KOHLENSTOFFS MIT EISEN, NICKEL, COBALT UND MANGAN

OTTO RUFF
Danzig-Langfuhr, Germany

Die elektrischen Vakuumöfen geben uns die Möglichkeit, Temperaturen bis zu etwa 2700° C zu erreichen und *konstant* zu halten. Mit der Schaffung dieser Oefen ist uns ein Temperaturgebiet für selbst quantitative Arbeit erschlossen worden, in dem bis dahin Versuche nur in rohester qualitativer Form möglich waren. Die Oefen haben den Nachteil, oberhalb etwa 2400° —2600° C. selbst bei bestem Vakuum mit den Dämpfen derjenigen Stoffe in merkbarer Konzentration erfüllt zu sein, die in ihnen als Heizwiderstände Verwendung finden—mit Kohlendämpfen von etwa 2600° ab im Falle der Kohlerohrkurzschlussöfen, mit Wolframdämpfen von etwa 2400° ab im Falle der Wolframrohrkurzschlussöfen. Ist das Vakuum in den Oefen weniger gut, so bilden sich im Kohlerohrofen, der Luft und Feuchtigkeit enthält, Kohlenoxyd, Cyan und Kohlenwasserstoffe in umso grösserer Konzentration, je schlechter das Vakuum und je höher die Temperatur ist; im Wolframrohrofen entsteht unter gleichen Bedingungen nur flüchtiges Wolframoxyd. Bei mässig gutem Vakuum, besonders in einer Wasserstoffatmosphäre und bis etwa 2400° scheint das Arbeiten im Wolframrohrofen deshalb günstiger zu sein als im Kohlerohrofen.

Die Konstruktion von Oefen mit Widerstandsrohren, die nicht aus Kohle oder Wolfram, sondern aus hochfeuerbeständigen Oxyden gefertigt sind, d.h. aus Massen ähnlich denjenigen, die in Nernstiften Verwendung finden, ist bis zu gleich hohen Temperaturen hinauf nicht möglich; denn die Schmelztemperatur des nach unserer Erfahrung höchst schmelzenden Oxydes, nämlich des Zirkonoxydes, liegt bei etwa 2550°. Da dieses

Oxyd, um die nötige Leitfähigkeit zu erhalten, noch mit Yttriumoxyd oder einem anderen Oxyd versetzt werden muss und da hierdurch sein Schmelzpunkt noch weiter herabgedrückt wird, so dürfte die in solchen Oefen erreichbare Maximaltemperatur 2250° kaum wesentlich überschreiten.

Die kohlende Wirkung der Atmosphäre unserer Kohlerohrkurzschlussöfen hat uns veranlasst, unter den vielerlei interessanten Aufgaben, die jetzt zur Lösung drängen, mit Vorsicht zu wählen und gemeinsam mit unsern Assistenten und Schülern zunächst vor allem die Bearbeitung solcher Stoffsysteme in Angriff zu nehmen, bei denen der Kohlenstoff selbst eine der Komponenten ist. Wir nahmen uns dementsprechend vor, einmal die Löslichkeit des Kohlenstoffs in den verschiedenen Metallen: Eisen, Nickel, Cobalt, Mangan, Vanadin, Niob, Tantal, Chrom, Molybdän, Wolfram, Uran, Titan und Zirkon in so weitem Temperaturbereich als möglich zu ermitteln, um auf solchem Weg zu den Grenzlinien der Temperatur-Konzentrationsdiagramme des Kohlenstoffs mit diesen Metallen zu gelangen, andererseits aber auch das Temperaturgebiet der Existenz der hierbei auftretenden Carbide nach Möglichkeit festzustellen.

Unsere in dieser Richtung bisher ausgeführten Versuche haben schon mancherlei hübsche Erfolge gezeitigt.

Die Grenzlinien der Systeme Eisen, Nickel, Cobalt, Mangan mit Kohlenstoff konnten bis zu den Temperaturen verfolgt werden, bei denen die an Kohlenstoff gesättigten Schmelzen unter 10 bis 20 mm Druck bezw. Atmosphärendruck verdampften.

Es hat sich auch gezeigt, dass die Bildung von Carbidformen, die nur bei höherer Temperatur beständig sind, bei niederer Temperatur unter Abscheidung von Graphit wieder zerfallen, eine ziemlich häufig sich findende Erscheinung ist. Nicht blos beim Eisen, bei dem dies gelegentlich früher schon angenommen, von uns aber zuerst eindeutig nachgewiesen worden ist, sondern auch beim Nickel, Cobalt, Wolfram, Molybdän und anscheinend noch manchen anderen Metallen bilden sich solche Carbide. Eine neue Entwicklung der Chemie der Carbide wird dadurch angebahnt.

Natürlich ist die Beobachtung, dass sich mit höherer Temperatur neue Verbindungsformen zeigen, welche bei niederer wieder zerfallen, in dieser allgemeinen Form nicht überraschend; denn sie steht im Einklang mit unseren theoretischen Anschauungen; aber im einzelnen vermittelt sie uns doch mancherlei neue Kenntnisse, die unsern Gesichtskreis wesentlich erweitern. Das nähere Studium dieser Carbide wird vor allem dann noch besonders interessant werden, wenn es gelingt, auch deren Molekulargrösse und Wertigkeitsverhältnisse klarzulegen; es sind dies Aufgaben, deren Bearbeitung wir gleichfalls in Angriff genommen haben.

Hier soll nur kurz über den derzeitigen Stand unserer Kenntnis von den Systemen Eisen, Nickel, Cobalt und Mangan mit Kohlenstoff berichtet werden, deren Temperatur-Konzentrationsdiagramme wir beistehend geben. 4 Figuren! Neu in diesen Diagrammen sind die Linien BDHY bezw. BDY, BY oder DY, welche die Grenzlöslichkeit der genannten Metalle in flüssiger Form für Graphit zeigen und die vorläufig nur gestrichelt geführten Linien YX bezw. YZ, welche die Siedetemperaturen aller Kohlenstoff haltigen Lösungen bezw. die obere Grenze der Existenzmöglichkeit aller *flüssigen* Lösungen andeuten.

Das Bemerkenswerteste an den Linien BDHY und BDY im Eisen und Nickelsystem ist die fast plötzliche Aenderung ihrer Richtung in den Punkten D und H.

Unregelmässigkeiten im Verlaufe der Löslichkeitslinie eines Stoffes müssen ihre Erklärung entweder in einer Aenderung der Natur des Bodenkörpers oder der Natur der Lösung finden. Es ist also die Frage zu erörtern, ob ein neuer Bodenkörper auftritt (derselbe könnte entweder ein neues Carbid oder eine neue Kohlenstoffmodifikation sein) oder aber, wenn dies nicht der Fall ist, ob die Aenderung der Zusammensetzung der Lösung eine entsprechende Aenderung der Löslichkeit des Kohlenstoffs nach sich ziehen kann.

Da wir immer in einem Graphittiegel und bis zu vollständig erreichtem Gleichgewicht gearbeitet haben, die Lösung an Kohlenstoff also stets gesättigt war, konnte die Bildung eines neuen Bodenkörpers neben Graphit in Form eines *festen* Carbids nur so eintreten, dass die *gesamte* Schmelze in dies feste Carbid überging—es sei denn, dass man metastabile Zustandsformen besonders grosser Haltbarkeit annehmen wollte. Ein

Festwerden der Schmelzen war bei keiner Temperatur zu beobachten.

Die zweite der oben genannten Möglichkeiten, das Auftreten einer neuen Kohlenstoffmodifikation fand ihre Erledigung durch die Untersuchung des Nickel-Kohlenstoffsystems. Nach dem Befund im Eisen-Kohlenstoffsystem müsste die Umwandlungstemperatur der beiden Kohlenstoffmodifikationen in einander entweder bei 1830° oder bei 2220° liegen; beim Nickel hätten wir sie bei ungefähr derselben Temperatur beobachten müssen; wir fanden eine rasche Aenderung der Löslichkeit aber nur bei ca 2080°.

Es bleibt also nichts übrig, als die Ursache für die Knicke[1] in der Aenderung der Zusammensetzung der Schmelzen selbst zu suchen. Dies scheint auch wirklich der Fall zu sein. Es lässt sich für den Punkt D des Eisen-Kohlenstoffdiagramms rein recht-rechnerisch zeigen, dass unsere Annahme gerechtfertigt ist.

Wir gingen bei unseren Rechnungen von folgenden Voraussetzungen aus:

1) Im Eisen-Kohlenstoffdiagramm verlaufen nachstehende Reaktionen neben einander und bedingen die Zusammensetzung der Schmelze.

a) $3Fe_{fl}+CC_{fest}\rightleftarrows Fe_3C_{fl}$—ca 15000 Cal
b) $2\ Fe_3C_{fl}+C_{fest}\rightleftarrows 3\ Fe_2C_{fl}$—ca 15000 Cal;

sie sind verbunden durch die Zwischenreaktion

C) $2\ Fe_{fl}+C_{fest}\rightleftarrows Fe_2C_{fl}$—ca 15000 Cal

Die Wärmetönungen sind ganz willkürlich angenommen; sie können ohne das Ergebnis im Prinzip zu ändern, in weiten Grenzen variiert werden. Der einfacheren Rechnung wegen betrachteten wir sie zwischen 1600° und 2150° als konstant.

2) Im Punkte D ist die Konzentration sowohl an Eisen als

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[1] Wir bezeichnen die Punkte D und H als "Knicke," obwohl wir uns dessen wohl bewusst sind, dass sie in grösserem Masstabe gezeichnet lediglich stärker gekrümmte Teile der Löslichkeitslinie darstellen. Man darf nicht vergessen, dass wirkliche Knicke, d. h. Schnittpunkte zweier Kurven auch beim Auftreten neuer fester Bodenkörper stets mehr oder weniger theoretische Abstraktionen sind, deren Zustandekommen den ideellen Grenzfall vorausgesetzt, dass die Bodenkörper nicht allmählich, sondern plötzlich ihre Zusammensetzung ändern, also vor allem keine feste Lösung miteinander bilden.

auch an Diferrocarbid eine sehr kleine; die letztere wird bei 1600° mit 0,1% Diferrocarbid und weniger angenommen.

3) Die Konzentration des freien, d, h, nicht gebundenen Kohlenstoffs ist in unseren Schmelzen zwischen 1600° und 2150° so klein, dass sie derjenigen des gebundenen gegenüber analytisch und thermisch zurücktritt. Wir führten sie bei 2150° mit etwa 0,05% in die Rechnung ein und liessen sie mit sinkender Temperatur ähnlich dem Dampfdruck logarithmisch fallen; (indem damit ein bestimmter Neigungswinkel für die Löslichkeitslinie des freien Kohlenstoffs angenommen wird, wird auch eine bestimmte Annahme über dessen Lösungswärme gemacht.)

Alle weiteren für die Rechnung nötigen Zahlengrössen sind dann einerseits durch die experimentell ermittelte Gesamtlöslichkeit des Kohlenstoffs, andererseits durch die Gleichung der Reaktionsisochore gegeben und willkürlicher Annahmen nicht mehr fähig.

Die Kurve, welche die Rechnung für 1600° bis 2150° ergibt, *deckt sich vollkommen mit der experimentell ermittelten* und mindestens die Möglichkeit des Zustandekommens eines solchen Knickes wie ihn Punkt D unseres Diagramms wiedergibt, ist damit erwiesen. Es lässt sich aber auch zeigen, dass der Knick D nur dann sich bilden kann, wenn die Zusammensetzung der Schmelze bei D ziemlich genau diejenige des Carbids Fe_3C erreicht.

Gilt nämlich unsere Voraussetzung 2 nicht mehr, nehmen wir z. B. an, dass die Schmelze bei 1600° statt 0,1% Fe_2C schon 1% Fe_2C enthalte, so verschwindet der Knick D aus unserer Löslichkeitslinie. Dasselbe geschieht auch, wenn der Gehalt der Schmelze an freiem Kohlenstoff ein wesentlich grösserer ist, als angenommen wurde. Das Vorhandensein des Knickes bei D lässt also auch umgekehrt wieder auf die Giltigkeit unserer Voraussetzungen 2 und 3 schliessen; die Analyse der Schmelze bei diesem Knick ergibt somit die Zusammensetzung der wichtigsten in ihr vorhandenen Molart um so genauer, je schärfer der Knick ist.

Das für den Punkt D im Eisen-Kohlenstoffsystem Gesagte hat ohne weiteres auch für die Deutung des Punktes D im Nickel-Kohlenstoffsystem Geltung, solange man die noch innerhalb der

Grösse der Versuchsfehler liegende Rückläufigkeit der Kurve ausser Betracht lässt.

Nicht ganz so einfach wie die Deutung des Punktes D gestaltet sich diejenige des Punktes H im Eisen-Kohlenstoffsystem; denn hier geht der Wert der Lösungswärme durch Null, indem er sein Vorzeichen wechselt. Während auf der Linie DH die Lösung des festen Graphits in der flüssigen Schmelze unter Wärmeabsorption erfolgte:

$$3\,\mathrm{Fe_{fl}} + \mathrm{C_{fest}} \rightarrow \mathrm{Fe_3C_{fl}} - \mathrm{x\ Cal\ und}$$

$$2\,\mathrm{Fe_3C_{fl}} + \mathrm{C_{fest}} \rightarrow 3\,\mathrm{Fe_2C_{fl}} - \mathrm{y\ Cal}$$

geschieht sie der Linie HY entlang unter Wärmeabgabe, etwa entsprechend der Gleichung:

$$3\,\mathrm{Fe_2C_{fl}} \rightarrow 2\,\mathrm{Fe_3C_{fl}} + \mathrm{C_{fest}} + \mathrm{z\ Cal}$$

Da sich die Lösungswärme des Graphits aus den 3 Grössen: *Schmelzwärme* des festen Graphits, *Lösungswärme* des geschmolzenen Graphits und *Reaktionswärme* des gelösten Graphits mit den in der Schmelze enthaltenen Molen zusammensetzt, so muss, da die Schmelzwärme und reine Lösungswärme des Graphits immer negativ sein dürften, die Reaktionswärme im Punkte H positiv sein und gleich der Summe der beiden erst genannten Wärmearten.

Zur Deutung des Punktes H genügt es darum nicht, bestimmte Annahmen über die Grösse der Wärmetönung der in der Schmelze zwischen den flüssigen Bestandteilen sich abspielenden Reaktionen zu machen; es ist auch nötig mit veränderlichen Wärmetönungen zu rechnen. Die Berechnungen werden dadurch etwas umständlicher und konnten deshalb bisher noch nicht befriedigend beendet werden. Nach dem zur Zeit vorliegenden Zahlenmaterial kann es keinem Zweifel unterliegen, dass die Rückläufigkeit der Löslichkeitskurve im Eisen-ev. auch Nickel-und Mangansystem mit einer durch die Aenderung der Wärmetönung bedingten Umkehrung der Reaktionen:

$$\mathrm{Metall_{fl}} + \mathrm{Graphit_{fest}} \rightarrow \mathrm{Carbid_{fl}}$$

erklärt werden kann; inwieweit man aus der Schärfe und Lage des Knickes auf die Existenz des von uns zunächst angenommenen Diferrocarbids schliessen kann, vermögen wir jedoch noch nicht zu übersehen.

Dem Triferrocarbid gleicht das Trinickelo- und Trimanganocarbid.

Beim Cobalt wurde ein dem Punkt D entsprechender Knick nicht gefunden. Die Carbidlösung siedet unter 20 mm Druck mit einem Kohlenstoffgehalt von etwa 6,7% bei etwa 2475°. In Wasserstoff von Atmosphärendruck kann man den Kohlenstoffgehalt der Schmelze noch etwas höher bringen, selbst über den für das Tricobaltocarbid verlangten Kohlenstoffgehalt von etwa 6,78% hinaus. Um dies anzudeuten, haben wir unseren Zahlen folgend die Kurve BY gestrichelt über Y hinaus noch etwas fortgesetzt. Aber die Schwierigkeiten, die wir der starken Nebelbildung wegen[1] bei der Temperaturbestimmung fanden, machen die ermittelten Zahlen unsicher, weshalb wir unsere Bestimmungen zu wiederholen gedenken.

Aus diesen Untersuchungen ergibt sich, dass es noch bis zu etwa 2500° hinauf fast ausschliesslich die Carbidgleichgewichte sind, welche die Lösung des Kohlenstoffs in unseren Metallen bedingen. Diese Gleichgewichte verschieben sich je nach der Richtung der Temperaturanderung im einen oder anderen Sinn. Der Kohlenstoffgehalt nimmt mit steigender Temperatur zu oder ab. BeimEisen sind es die beiden Reaktionen:

$$3\,Fe_2C_{fl} \rightarrow 2\,Fe_3C_{fl} + C_{fest}$$

$$2\,Fe_3C_{fl} \rightarrow 3\,Fe_{fl} + C_{fest}$$

welche unterhalb 2220° mit sinkender Temperatur von links nach rechts sich verschiebend *die Lage des Gleichgewichts bestimmen.* Ueber 2220° dürfte die Verschiebung des Gleichgewichts in umgekehrter Richtung erfolgen.

Beim Nickel verschiebt sich von 2080° abwärts das Reaktionsgleichgewicht:

$$Ni_3C_{fl} \rightarrow 3\,Ni_{fl} + C_{fest}$$

von links nach rechts und beim Cobalt ist es wahrscheinlich ebenso.

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[1] Die Nebelbildung ist um so stärker, je höher die Versuchstemperatur ist; sie tritt ebenso wie bei Gegenwart von Wasserstoff in unseren Oefen auch bei Gegenwart von Stickstoff ein und ist durch das Temperaturgefälle im Ofen bedingt. In dessen heissesten Teilen bilden sich Kohlenstoff reichere Verbindungen, die in den kälteren unter Ausscheidung von Kohlenstoff der eben den Nebel bildet, wieder zerfallen.

Beim Mangan aber beobachten wir die umgekehrte Folge:

$$3\,\mathrm{Mn}_{\mathrm{fl}} + \mathrm{C}_{\mathrm{fest}} \rightarrow \mathrm{Mn}_3\mathrm{C}_{\mathrm{fl}}$$

Der Aenderung des Reaktionsverlaufes entsprechen nach Vorzeichen und Grössenordnung ungefähr auch die von uns gemeinschaftlich mit Gersten experimentell bestimmten Wärmetönungen des Triferro-, Trinickelo-und Trimanganocarbids.

Wir fanden für:

$$\mathrm{Fe_3C} - 15{,}6 \text{ Cal}; \quad \mathrm{Ni_3C} - 394 \text{ Cal}; \quad \mathrm{Mn_3C} + 12{,}9 \text{ Cal.}^{1}$$

Die für das Trinickelocarbid gefundene Wärmetönung kann nur einen ungefähren Masstab für deren wirkliche Grösse abgeben, da Nickelreguli mit grösserem Gehalt an Trinickelocarbid als etwa 5% nicht herzustellen sind und die Wärmetönung an solchen Präparaten bestimmt werden musste.

Da der Bildungswärme fester Stoffe die Affinität der in ihnen verbundenen Elemente ungefähr parallel geht, so findet in diesen Wärmetönungen auch die ausserordentlich geringe Beständigkeit des Trinickelocarbids, die etwas grössere des Triferrocarbids und die relativ grosse des Mangancarbids ihre Erklärung.

Besonderes Interesse bieten noch die Verhältnisse, die wir beim Sieden unserer Carbidschmelzen fanden. Die abziehenden Dämpfe von den an Kohlenstoff gesättigten Schmelzen des Mangens, Nickels und Cobalts enthielten nur äusserst wenig Carbid; ihr Gehalt an Kohlenstoff lag innerhalb der Grenzen der Versuchsfehler und im Rückstand hinterblieb etwa diejenige Menge Graphit, die der vorher in der Schmelze gelösten Kohlenstoffmenge entsprach. Nur beim Eisen waren wir der zu hohen hierfür nötigen Temperatur wegen bisher nicht in der Lage, gleiche Bestimmungen auszuführen; doch haben wir uns durch Destillation im Lichtbogen auch bei diesem davon überzeugt, dass beim Verdampfen seiner an Kohlenstoff gesättigten Lösung unter vermindertem Druck der grössere Teil des ursprünglich gelöst gewesenen Kohlenstoffs als Graphit hinterbleibt.

Wir haben deshalb die Punkte Z, welche die Zusammensetzung der Dämpfe angeben sollen, die mit der flüssigen an Kohlenstoff

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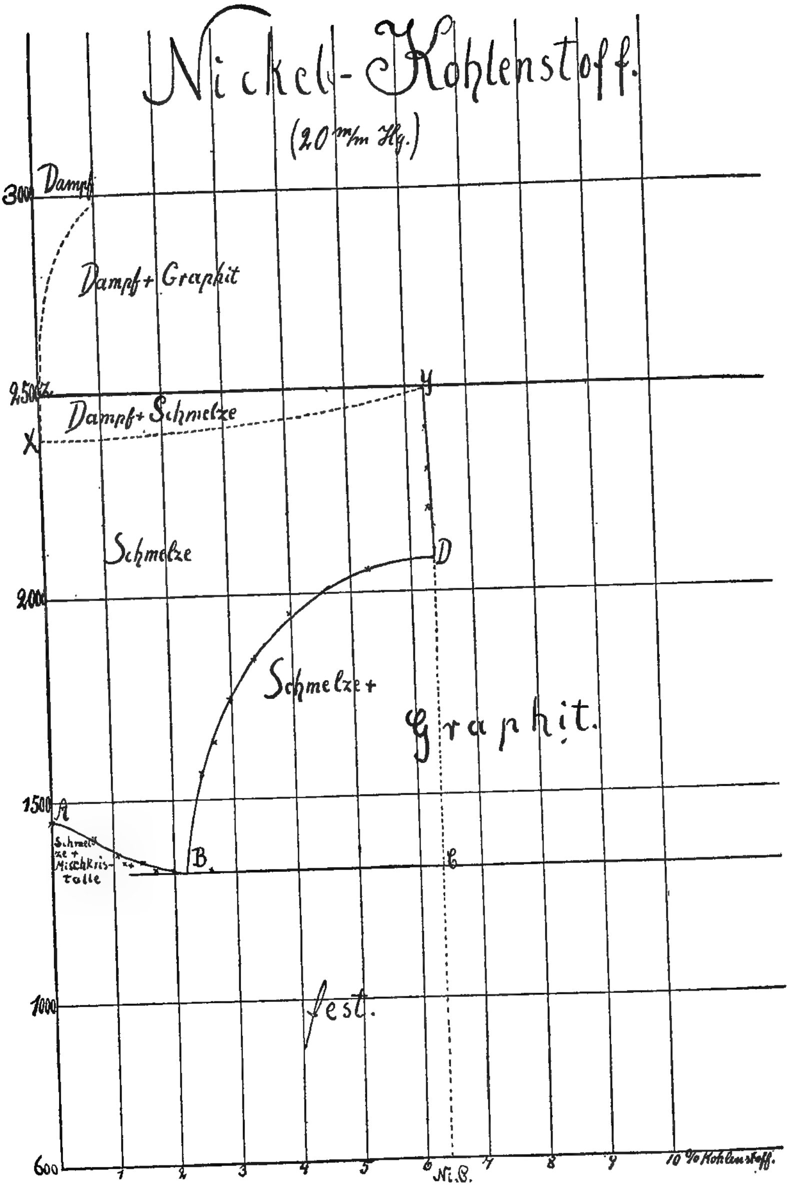
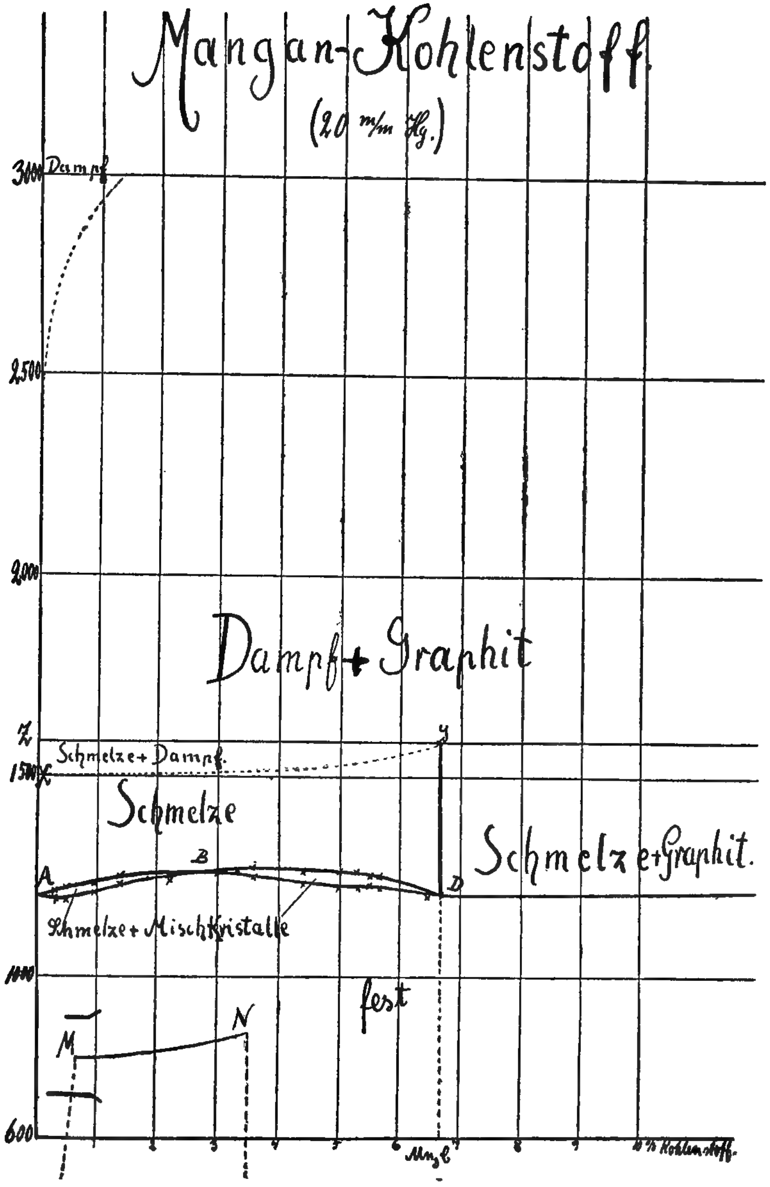
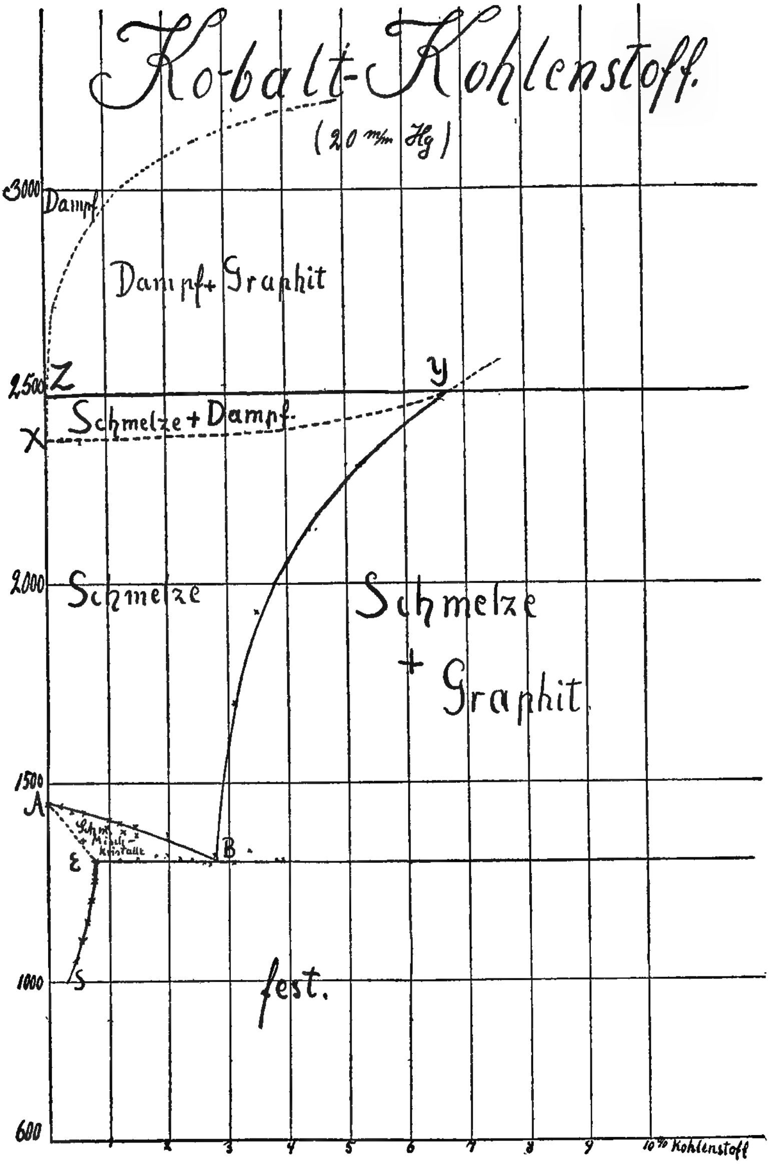
[1] In Übereinstimmung mit Le Chateliers Bestimmung.

gesättigten Lösung im Gleichgewicht sind, bis dicht an die Ordinatenachse für Kohlenstoff herangerückt.

Ist unsere Beobachtung am Eisen richtig, so bringt sie die Erklärung für manche andere, vor allem wird die merkwürdige Tatsache, dass die Kohlung des im Elektrostahlofen befindlichen Eisens immer nur minimal ist, obwohl der Lichtbogen an Kohleelektroden gebildet wird, verständlich; denn der Dampf, der den Lichtbogen leitet, besteht aus fast reinem Eisen. Unsere Beobachtungen sind auch ein weiterer Beleg dafür, dass die Kohlung unserer Metalle selbst noch bei Temperaturen bis zu etwa 2500° im wesentlichen nur durch die Vermittlung von Kohlenoxyd oder durch direkte Berührung von Metall und Kohlenstoff, nicht aber durch Kohlenstoffdampf herbeigeführt wird.

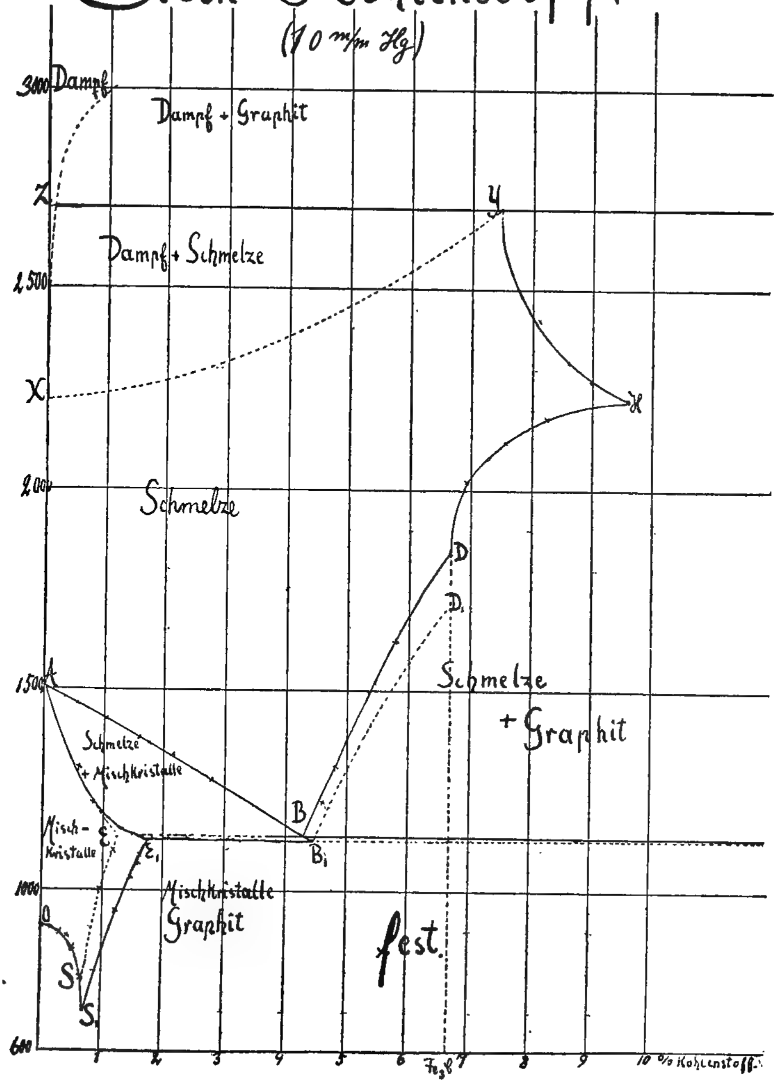

Nickel-Kohlenstoff.
(20 m/m Hg.)
3000
Dampf
Dampf + Graphit
2500 K.
Y
Dampf + Schmelze
X
Schmelze
D
2000
Schmelze + Graphit.
1500
A
Schmelze + Mischkristalle
B
C
1000
fest.
600
1
2
3
4
5
6
Ni.C.
7
8
9
10 % Kohlenstoff.

Mangan-Kohlenstoff
(20 m/m Hg.)
3000 Dampf
2500
2000
Dampf + Graphit
Z
y
Schmelze + Dampf
1500 X
Schmelze
Schmelze + Graphit.
B
A
D
Schmelze + Mischkristalle
1000
fest
N
M
600
1
2
3
4
5
6
Mn3C
7
8
9
10 % Kohlenstoff.


Kobalt-Kohlenstoff.
(20 m/m Hg)
3000
Dampf
Dampf + Graphit
Z
Y
2500
Schmelze + Dampf
X
2000
Schmelze
Schmelze + Graphit
1500
A
Schm. + Misch-kristalle
B
E
1000
S
fest.
600
1
2
3
4
5
6
7
8
9
10 % Kohlenstoff

Eisen-Kohlenstoff.

(10 m/m Hg)



SUR LA NOMENCLATURE DES SELS COMPLEXES DE LA CHIMIE MINERALE

G. Urbain

Professeur à l'Université de Paris, Paris, France

§1—La commission française de Nomenclature pour la Chimie Minérale a pensé que des réformes n'étaient pas également urgentes pour toutes les classes de composés.

Si les dénominations actuellement en usage pour les composés les plus simples ne sont pas toujours rationnelles ni même heureuses elles sont du moins assez familières aux chimistes pour que ceux-ci ne risquent pas de faire des confusions parmi les substances qu'elles désignent.

La commission abordera cette question dans la mesure ou il sera nécessaire de rompre avec des traditions surannées, mais elle évitera autant que possible de modifier les noms acceptables que l'usage a consacré.

En ce qui concerne les combinaisons complexes, il n'y a aucune tradition à ménager. La question est des plus confuses et sa solution est urgente. La commission française l'a étudiée d'une façon spéciale en s'inspirant des considérations suivantes.

§2—Toute nomenclature doit avoir pour point d'appui une classification. D'autre part, les classifications reflétaient généralement des théories. Or la Chimie Minérale a fait dans ces vingt dernières années des progrès théoriques considérables qu'elle doit au remarquable développement de la Chimie Physique.

La place prépondérante qu'occupent les électrolytes, grâce à l'importance particulière du dissolvant "eau" justifie le développement considérable qu'ont pris les théories Electrochimiques.

Le langage de la théorie des ions tend de plus en plus à se substituer au langage ancien. L'opposition que les idées de Svante Arrhénius ont rencontrée au début a presque complètement disparue. Les ions ont droit de cité dans l'enseignement officiel.

Les sels résultent de la juxtaposition des ions. Même si l'on n'admet pas la théorie des solutions diluées, on est conduit par la notion de substitution à considérer tout ion complexe comme un bloc, c'est-à-dire comme un radical: tel est le cas pour l'ion Ammonium (NH^4).

Abstraction faite des désinences, tout sel est actuellement désigné par les ions qui le composent. On ne dit plus Chlorhydrate d'ammoniaque, mais chlorure d'ammonium. Nommer les sels revient à juxtaposer les noms des ions dont ils sont constitués. Dans le cas des sels simples aucune difficulté ne se présente; mais il n'en est pas toujours ainsi dans le cas des sels complexes.

§3—SELS COMPLEXES.

Tout sel complexe peut être considéré comme résultant de la juxtaposition d'ions de signes contraires dont l'un au moins, serait un ion complexe. C'est la un point de vue très moderne.

Autrefois tout sel complexe était considéré comme résultant de la juxtaposition de molécules salines plus simples. Cette conception était conforme à la théorie dualistique de Berzélius: tout sel complexe était alors considéré comme un sel double.

La question qui nous occupe, comporte dans le domaine de la Chimie Organique, un précédent historique. Doit-on, en Chimie Minérale, substituer les notations unitaires aux notations dualistiques, comme on l'a fait en Chimie Organique à l'instigation des Laurent et Gérardt? Doit-on considérer la Carnallite comme un magnéso-chlorure de potassium et la formule ($MgCl^3$) $K \div 6H^2O$; ou doit-on considérer le platocyanure de potassium comme un cyanure double de platine et de potassium et le formuler: $Pt\ (CN)^2,\ 2KCN$?

Si l'on croit nécessaire d'adopter pour les électrolytes un système uniforme de nomenclature, il faut choisir. Le choix, quel qu'il soit, sera arbitraire, car les deux manières de voir seront défendables et également justifiées par les faits.

La solution de Carnallite peut renfermer parmi beaucoup d'autres choses, des ions ($Mg-Cl^3$) de même que l'on peut admettre que la solution de platocyanure de potassium renferme quelques molécules de Cyanure platineux Pt $(CN)^2$ et quelques molécules de Cyanure de potassium.

Toutefois les exemples précédents ont été choisis de telle sorte qu'il semblera préférable à tout chimiste de formuler la Carnallite Mg Cl^2, K Cl, $6H^2O$ et le platocyanure de potassium (Pt $(CN)^4$)K2.

En effet la Carnallite se comporte en solution, principalement, comme un mélange de Chlorure de Magnésium et de Chlorure de potassium et d'eau. Ces trois corps, dans les phénomènes d'équilibre dont ce système est le siège, doivent être considérés comme des constituants indépendants.

Au contraire dans le platocyanure de potassium, le platine aussi bien que le cyanogène sont masqués à leurs réactifs habituels et dans la solution de ce complexe on ne peut révéler ni la présence du cyanure de potassium, ni celle du cyanure platineux.

Sans doute on peut concevoir que l'ion (Pt-$(CN)^4$) est partiellement dissocié en ion (CN) et Pt Cl^2, à la façon dont l'ion (Mg$-$$Cl^3$) est dissocié en ion *Cl* et $MgCl^2$. Dans le premier cas la dissociation serait très faible; elle serait considérable dans le second. Il n'y aurait alors entre les deux ions complexes qu'une différence de degré de leur dissociation.

Cette manière de voir serait incontestablement correcte, si le platocyanure de potassium en solution était un système d'équilibre stable, comme c'est le cas dans la Carnallite en solution.

Mais c'est là seulement une possibilité et il n'est pas nécessaire qu'il en soit ainsi. Bien plus, il est tout à fait probable, qu'en solution, le platocyanure de potassium constitue un système métastable.

On sait que les formes métastables peuvent subsister sans se transformer nécessairement en formes plus stables à la faveur d'une rigidité particulière de leur architecture moléculaire qui s'oppose aux transpositions. Lorsqu'un tel cas se présente en thermodynamique, on dit que le système est maintenu par des liaisons dans un état d'équilibre contraint. Une forme métastable est réellement un système en état de contrainte chimique. J'attire l'attention sur ce point: La contrainte chimique est extrêmement fréquente et pour ainsi dire la règle dans le cas des complexes des métaux les moins électropositifs. Elle est tout à fait exceptionnelle dans le cas des complexes des métaux les plus électropositifs.

Il est nécessaire de développer cette proposition qui me parait avoir une certaine importance.

Tout complexe peut être considéré comme un système. Or un système n'admet en général, dans des conditions fixées de température, de pression ou de concentration, qu'un seul état d'équilibre stable.

Dans ces conditions, un système de constituants en nombre limité, ne pourra donner naissance qu'à un nombre restreint d'espèces chimiques d'une composition déterminée. Ces espèces pourront à la faveur des réactions reversibles se transformer les unes dans les autres.

C'est bien ainsi que les choses se passent pour un métal relativement très électropositif comme le magnésium; mais il est évident qu'il n'en est pas de même pour le platine ou même pour le cobalt dans ses combinaisons trivalentes.

Considérons pour fixer les idées le système qui admet la composition:

$$\text{Co}\,(\text{NO}^2)^3,\ 3\ \text{NH}^3.$$

A Werner a montré qu'il existait 7 complexes cobaltiques de cette composition. Or ces complexes subsistent en solution, dans des conditions absolument identiques. Il est bien évident qu'ils ne peuvent alors être tous les 7 en état d'équilibre stable. Ces 7 isomères ne peuvent subsister qu'à la faveur de la contrainte chimique: ce sont des espèces métastables pour lesquelles il n'y a pas lieu d'admettre une décomposition partielle en ammoniaque libre et nitrate cobaltique, si légère qu'elle soit. En effet à la faveur de cette décomposition partielle, les 7 isomères de Werner pouvaient se transformer les uns dans les autres par une série de modifications progressives infiniment petites de l'état d'équilibre. Or on n'observe rien de semblable. Ces espèces peuvent exister indéfiniment en présence de leur solution commune pour former un complexe de phases auquel la loi des phases ne s'applique pas pour cette excellente raison que le nitrite cobaltique et l'ammoniaque ne peuvent être considérés dans ce cas comme un système de constituants indépendants. Il est démontré de cette manière, en s'appuyant sur les principes rigoureux de la thermodynamique, que les molécules composantes de certains complexes ne se comportent en aucune manière comme des constituants indépendants, d'un système de phases juxtaposées. Je propose de désigner de tels complexes du nom de complexes parfaits, pour les distinguer des sels doubles proprements dits, qui tels que la Carnallite admettent comme molécules composantes des corps qui, dans un complexe de phases ayant la composition du sel double, sont des constituants indépendants du système.

Aux sels doubles proprement dits conviennent des formules dualistiques, aux complexes parfaits des formules unitaires.

Cette classification de la représentation des sels complexes qui s'en suit, sont les plus conformes aux théories dominantes de la Science actuelle. Ce n'est pas un système rigide prétendant plier sous une règle unique tous les sels complexes.

La question n'est plus de faire un choix entre le système unitaire et le système dualistique. En Chimie Organique le premier a triomphé et le second a été banni—sauf en ce qui concerne les combinaisons dites moléculaires. C'est qu'en vérité les espèces de la Chimie Organique sont, d'une manière générale, des espèces en état de contrainte chimique. Hantzsch puis Vant' Hoff ont fait remarquer en effet que la chimie organique était une chimie de systèmes métastables.

Les espèces stables de la Chimie du carbone sont le charbon, le gaz carbonique, quelques carbures et les substances qui entrent dans la composition des goudrons.

C'est à la contrainte chimique que la chimie organique doit sa physionomie si spéciale; la multiplicité de ses espèces et la fréquence de ses cas d'isomérie.

Mais la chimie organique ne jouit pas exclusivement de ce privilège. Tel est aussi le cas pour la chimie de l'or, des métaux de la famille du platine et des métaux du groupe du fer sous la forme trivalente.

Tous ces éléments ont le caractère commun de jouir d'une électro affinité très faible. A mesure que l'on descend dans la hiérarchie des métaux, la tendance à la contrainte chimique s'évanouit. Elle est sensiblement nulle dans le cas des métaux alcalins, des métaux alcalinoterreux et des Terres Rares. Les métaux de la série magnésienne, puis le Cuivre et le Mercure forment la transition.

Les complexes des métaux peu électropositifs sont en général des complexes parfaits; les métaux de la série magnésienne sont des sels doubles proprements dits. La chimie des sels complexes se modifie progressivement dans le sens qui vient d'être indiqué quand on étudie successivement les métaux dans l'ordre de leur électroposivité croissante.

La manière de voir qui consiste à considérer l'alcool comme une combinaison d'éthylène et d'eau a été rejetée d'une manière définitive par les chimistes organiciens. Les mêmes raisons peuvent être invoquées pour rejeter la manière de voir qui ferait considérer le platocyanure de potassium comme un sel double. L'ion platocyanure ($Pt=(CN)^4$) est un bloc, un radical au même titre que l'Ethyle C^2H^5.

Au contraire les sels doubles sont de véritables "combinaisons moléculaires." Cette expression prend d'ailleurs, dans les considérations thermodynamiques qui précèdent, un sens incomparablement plus précis que celui que lui a été attribué jusqu'ici.

En Chimie Organique, les combinaisons moléculaires sont l'exception et on les néglige systématiquement. En Chimie Minérale, on ne peut les négliger vu leur grand nombre; mais ce serait une erreur de les considérer comme la règle ou de considérer comme telle les complexes parfaits. Entre les sels doubles indiscutables et les complexes parfaits indiscutables, il existe toute une série de complexes formant la transition. Dès lors notre classification n'est pas rigoureuse. Nous le reconnaissons bien volontiers.

Mais y-a-t-il des classifications rigoureuses?

Au cours de ses discussions, la commission française de nomenclature pour la chimie minérale a reconnu qu'aucune classification n'était rigoureuse. Entre toutes les classes concevables de composés, il existe des termes de transition. Dans cet ordre d'idées il semble vain de chercher à définir. Les définitions ne donnent que l'illusion de la rigueur en matière de classifications et il est impossible d'en citer une qui ait résisté à l'examen.

La distinction entre les acides et les bases est singulièrement compromise par l'existence d'oxydes amphotères tels que l'Alumine et l'oxyde de Zinc, la distinction entre les métaux et les métalloïdes est illusoire.

La règle consiste à rapprocher ce qui se ressemble le plus. Or, en chimie rien n'est plus aisé que de faire surgir des analogies pour le besoin des causes les moins défendables. La commission n'a pas voulu tomber dans ce travers. Elle a décidé de ne pas s'arrêter à discuter les cas douteux. Elle admet qu'un complexe difficile à classer, soit parmi les sels doubles, soit parmi les sels complexes parfaits, puisse être indifféremment considéré comme l'un ou comme l'autre, ce qui correspondra à deux manières de les nommer. L'inconvénient n'aura pas de conséquence grave pourvu que, quelque soit le nom préconisé, il n'y ait aucun doute sur l'individualité de l'espèce désignée.

Les considérations qui précèdent justifieront, je l'espère les conclusions que le rapporteur de la commission française, Monsieur F. Bourrion a consigné dans son rapport présenté à l'Association internationale des Sociétés Chimiques qui accompagne ce mémoire.

MICROGRAPHIE DES FONTES SPECIALES POUR BAGUES DE PISTONS

ROBERT ADAN

Docteur en sciences chimiste—métallurgiste à Gand Belgique, Ghent, Belgium

On sait toutes les difficultés qu'il y a à trouver une bonne composition pour la fabrication des bagues de piston. La théorie de cette fabrication a été plusieurs fois étudiée, aussi sans vouloir nous étendre sur les questions de dureté et d'élasticité à observer, nous voudrions présenter au Congrès le résultat de notre pratique industrielle sur quelques cas prélevés dans ce domaine.

L'analyse chimique a servi de base pour l'achat des matières premières et pour la marche des opérations d'affinage de la fonte. L'application du microscope suivie de l'examen métallographique nous a permis de reconnaître les conditions de traitement à observer et nous a permis de supprimer presque complètement les essais pratiques des pièces terminées. Elle n'autorise peut être pas la suppression complète de ces essais, mais elle permet d'en réduire considérablement le nombre en éliminant a priori un grand nombre de produits dont elle établit par avance la mauvaise qualité.

Les pièces de fonte fournies comme ressorts sont souvent ou trop tendres, douces à l'usure et exigent un remplacement fréquent, ou trop dures, elles usent alors le manchon des cylindres ce qui nécessite des révisions coûteuses.

On a préconisé dans ces derniers temps l'emploi de fontes dures très siliceuses. Le silicium localise et nourrit les particules de graphite éparpillées à travers le métal. Ces parcelles de graphite se localisent dans certaines portions où leur distribution est irrégulière et elles affaiblissent sérieusement le métal en le rendant extrêmement dur et cassant. Les expériences faites à l'aide de ces compositions, en opérant sur un grand nombre de types divers ne nous ont pas donné de résultats satisfaisants pour continuer les recherches en ce sens.

Au cours de ces recherches notre attention a été amenée sur une composition intermédiaire entre la fonte pour la fabrication de l'acier basique et les fers de forges anglais. Il a une teneur moyennement élevée en phosphore.

Sa teneur en manganèse est également élevée: de 0.750 1.50%. La teneur en soufre varie habituellement de 0.06 à 0.10%. C'est probablement la combinaison des teneurs élevées en phosphore et en manganèse qui donne à ce fer sa cassure caractéristique fine et grenue.

La matière première est généralement de la composition indiquée ci-dessous. Souvent la teneur en phosphore est plus élevée et celle en manganèse atteint 1.5%. Par la fusion successive on l'amène à la composition moyenne de 3^e fusion indiquée par le tableau en suivant en même temps les modifications au moyen du microscope.

Dosages	1^e. Fusion	2^e. Fusion	3^e. Fusion
Carbone graphitique	3.18	2.75	2.49
" combiné	0.31	0.42	0.61
Silicium	2.79	2.25	1.53
Manganèse	1.26	0.71	0.63
Phosphore	0.37	0.36	0.34
Soufre	0.04	0.06	0.079

Comme on le voit la refonte a pour effet d'enlever le silicium et d'augmenter la teneur en soufre. Elle se traduit en fin de compte par la transformation du métal en une sorte de fonte blanche à grains serrés. Une teneur en phosphore élevée n'est pas nuisible pour cet usage à condition de ne pas dépasser 1% environ. Une forte proportion du carbone primitif se trouve à l'état de combinaison. L'obtention de cette texture serrée, l'oxydation du silicium et du carbone graphitique est facilitée par l'emploi de faibles quantités de thermite.

Le photogramme 1 représente la masse grenue de carbure de fer (cémentite Fe_2 C) corrodée par l'acide picrique, parmi laquelle se trouvent répandues les dunes de perlite, entourant des flots de cémentite et de ferrite. Le graphite apparaît en grandes paillettes, les dunes de perlite sont disposées en stries parallèles. On perçoit dans ce photogramme les constituants de la fonte grise, perlite et ferrite, graphite et phosphure de fer.

Le photogramme 2 montre de grandes plages blanches de ferrite presque pure et des îlots de cémentite bien découpés, entre ceux-ci s'estompent en grisailles des champs de perlite se détachant sur un fond clair de ferrite. On distingue aussi trois grandes lamelles de graphite dont une partie se trouve dans la ferrite blanche tandis que l'autre est engagée dans la perlite grise. A gauche, un grand trou noir : c'est une trace de scorie qui s'est probablement échappée pendant la coulée. L'examen micrographique fait constater la présence de fonte blanche mêlée de fonte grise propre à la conversion en fer forgé : c'est une excellente composition pour la fabrication des cercles de pistons. L'analyse chimique en est donné dans le tableau précédent sous "3^e. fusion."

Le photogramme 3 représente une partie isolée du photogramme 2 sous une amplification de 500 diamètres mais sans l'emploi d' aucun réactif d'attaque. Le graphite se présente sous forme de petites lamelles allongées et irrégulières et aussi en groupes de points de différents diamètres. Ces grandes paillettes notres sont entourées de plages blanches non différenciées par l'attaque. Espacées dans la préparation, on aperçoit de petites taches blanches disséminées irrégulièrement. Cette particularité du photogramme nous a amené à en rechercher chimiquement les causes, nous avons trouvé ainsi qu'elles étaient dues à des cristaux de ferro-aluminium. L'analyse chimique nous fit découvrir des proportions variant entre 0.32 et 0.39 d'aluminium pour cent. Sa présence, sans aucun doute, échappe à l'attention, si le microscope n'avait décelé cette impureté.

J'ai choisi parmi un grand nombre cet exemple emprunté à la pratique de l'usine et se rapportant au traitement d'une seule composition. Les cas analogues sont nombreux, mais je crois par l'examen d'un seul avoir mieux fait comprendre l'intérêt qu'il y a à suivre au microscope et au laboratoire le résultat d'une étude faite en grand par l'industrie. Ce qui précède montre que la fabrication des bonnes bagues de pistons n'est possible que sous le contrôle de la micrographie.

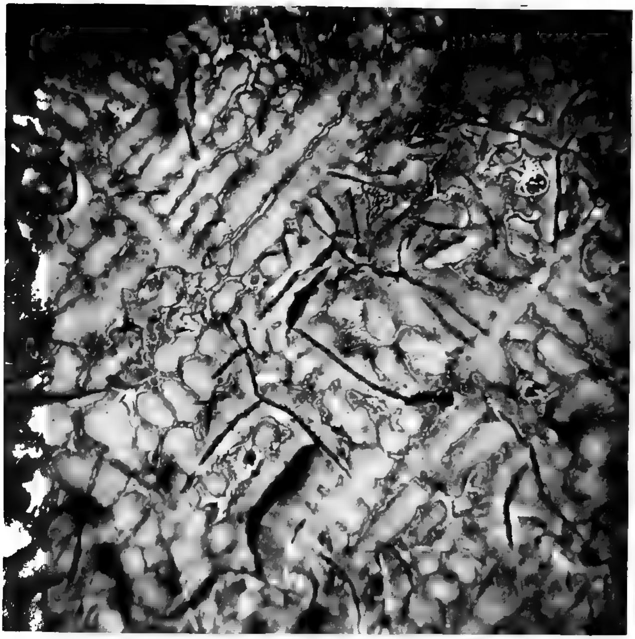


Figure 1

Figure 2

Figure 3

(*Abstract*)

ERRORS IN GAS ANALYSES RESULTING FROM THE ASSUMPTION THAT THE MOLECULAR VOLUMES OF ALL GASES ARE ALIKE

George A. Burrell and Frank M. Seibert

The authors submit actual calculations from gas analyses they have performed in which is shown the need for correcting well known equations so that the errors which result from the assumption that the molecular volumes of all gases are alike will not occur.

The best density determinations made of the common gases were chosen, and the reactions for complete combustion with oxygen of carbon monoxide, methane, ethane, propane, etc., were changed accordingly.

The combustible constituents in natural gases are changed in some cases as much as two per cent when the correct equations are used.

The application of the study consists in the use of the corrected equations when analyses are made of gas mixtures containing high percentages of combustible gases.

ELECTRIC HEATING AND THE REMOVAL OF PHOSPHORUS FROM IRON

Albert E. Greene
Chicago, Ill.

Processes for the removal of phosphorus from iron or steel are steadily assuming greater importance in view of the abundance of high-phosphorus iron-ore and the diminishing supply of pure ore. In the present processes of removing phosphorus, by the basic open hearth or basic Bessemer, or even electric processes, complete control over the metal metallurgical conditions is either impossible or has not yet been realized. The removal of phosphorus has so long been accomplished along certain well defined lines that when the electric furnace made its appearance, metallurgists stuck to the same old reactions used in the older processes and failed to appreciate and take advantage of the new forces at their disposal. It is an object of this paper to set forth more clearly the metallurgical reactions by which phosphorus can be removed from iron and to show the necessity of controlling the conditions and particularly the temperature by means other than combustion in the furnace chamber.

Invariably the commercial removal of phosphorus has been accomplished by oxidation. The reactions involved in oxidation of phosphorus in general consist first of the formation of P_2O_5; and, second, the combination of this oxide with lime forming calcium phosphate, which latter is held in a slag high in oxide of iron. In the present used processes, the phosphorus is never removed without the assistance or presence of considerable quantities of oxide of iron. The oxygen for removal of phosphorus in the basic open hearth process comes largely through the medium of oxide of iron and partly from the furnace gases but not from lime, and the lime itself cannot prevent the reduction of phosphorus back into the metal out of slags from which oxide of the iron is largely reduced, and likewise in the Basic Bessemer process, although here the oxygen comes originally from air, yet oxide of iron formed in the blow is the essential carrier of oxygen.

Among the more important metallurgical conditions which control the reactions of phosphorus are the temperature, the presence of oxidizing agents or reducing agents, or both, and the intensity of the resulting oxidizing or reducing conditions, or, in other words, the equilibrium conditions governing the reactions involving oxygen; the influence of slags, including the influence of oxides therein having affinity for oxide of phosphorus, or other phosphorus compounds, the solubility in the slag of such phosphorus compounds, the presence of oxides of like chemical nature to phosphorus oxide and tending to displace it; and the affinity of the reduced metal for phosphorus. In processes where the heat is supplied by combustion, it is not possible to maintain complete control over all the above conditions. In the open hearth furnace, the temperature is maintained by combustion of gas in the furnace chamber and the atmosphere is oxidizing to a greater or less extent. Any control over the reducing conditions in an open hearth furnace must therefore come from reducing agents in the metal and very limited control, if any, can be had over the action of these agents such as silicon or dissolved carbon. Since oxide of iron cannot be kept from forming in the slag under influences of the furnace atmosphere, it is apparent that the silicon or carbon in the metal are the agents which must be relied upon to prevent such oxidation.

To hold the strongly acid oxide of phosphorus in the slag requires a fluxing agent having strong affinity for phosphorus and which is strongly basic in chemical nature, like lime. Calcium phosphate is not at all difficult to reduce, however, at an elevated temperature and with strong reducing agents and either silicon or carbon is capable of reducing it. This statement holds true even though the carbon or silicon be dissolved in iron, although the intensity of the reducing action is then less, possibly owing to the "pulling action" of the iron itself on these reducing elements. The temperature may, of course, greatly influence the action on the slag of these reducing agents contained in the metal and may so change their affinity for oxygen as to prevent reduction of certain oxides in the charge, as is so in the case between carbon and phosphorus. In an open hearth furnace, calcium phosphate will be reduced from the slag back into the metal when the conditions of equilibrium between the oxides of iron in the slag and the reducing agents in the metal are such as to reduce the amount of iron-oxide below a certain limit. Silicon is such a strong reducing agent that practically always, except in certain cases to be noted later, it must be oxidized out of the metal before the phosphorus is attacked. If present in the bath, it reacts with any oxide of phosphorus present and reduces it. The presence of large amounts of silica in the slag or lining of the vessel is ordinarily detrimental to removal of phosphorus.

The influence of carbon, the other important reducing agent in the metal, is largely dependent on the temperature, its affinity for oxygen being less than that of phosphorus at low temperatures, and vice versa at temperatures above about 1450°C. Thus, at low temperatures, carbon dissolved in the iron is not a strong enough reducing agent to reduce calcium phosphate held in a slag high in oxide of iron, but at higher temperatures it is. Thus, either by means of silicon or by means of carbon contained in the metal or, of course, by solid carbon, the oxide of iron in the slag may be readily reduced and when such reduction proceeds far enough, the calcium phosphate is also reduced and the phosphorus goes back into the metal.

The fact that at low temperatures phosphorus is more easy to oxidize out of the metal than carbon is the basis of several modifications of the open hearth process, such as the Krupp washing process, the Bertrand-Thiel process, etc. The slight differences in these processes, such as the heating up of ore, lime, and pig iron, together, or the preliminary heating of the ore and lime and subsequent use of molten pig iron, do not change to any great extent the final result as to the method of removing phosphorus. The manner of carrying out this oxidation of phosphorus determines the degree of activity and frothiness of the slag, but essentially the reaction is the formation of calcium phosphate in the presence of considerable oxide of iron.

In the operation of the Basic Bessemer process, the chemical reactions involved in the separation of phosphorus are in reality practically the same as those in the open hearth process. In the Bessemer process, temperature is maintained by combustion as in the open hearth, the combustible materials being the silicon, phosphorus, iron, carbon, etc., of the charge, and also these are burned with an excess of oxygen to produce the necessary heat. Oxidation of the phosphorus results from oxygen of air primarily, but oxide of iron formed from the air acts as a carrier of oxygen just as in the open hearth process the slag serves as a carrier of oxygen from the furnace gases.

A large proportion of the heat evolved in the Basic Bessemer process results from the oxidation of phosphorus, but it has been found that a certain proportion of silicon is necessary in the pig iron to produce the requisite final temperature. Silicon is oxidized first, together with iron, and thereby the temperature of the bath is raised above that known as the critical temperature between carbon and phosphorus, and above this critical temperature the phosphorus is not removed appreciably until after both the silicon and the carbon are largely oxidized out. In certain cases with low silicon, oxidation of phosphorus takes place from the early part of the blow simultaneously with that of carbon. This is what would be expected if the temperature be held at about the critical point since at this temperature the oxidation of carbon and the formation of calcium phosphate take place with equal readiness.

An interesting example of the effect of metallic reducing agents in connection with the Basic Bessemer process is the rephosphorization of the metal on the addition of spiegel. The spiegel enters the metal at a high temperature and through a slag containing considerable quantities of calcium phosphate. At an elevated temperature, both silicon and manganese are easier to oxidize than phosphorus and these two elements tend to reduce the phosphorus from the slag back into the metal. From recent experiments of the writer, it has been found that at a low temperature, phosphorus is, on the contrary, more easily oxidizable than manganese in the presence of lime and can be separated as calcium phosphate without oxidation of manganese. The reactions involved will be more fully discussed later.

On comparison of the conditions in the Bessemer and Open Hearth process, it is seen that the controlling factors in the separation of phosphorus are almost identical. Lime is, of course, necessary to hold the phosphorus in the slag. Combustion is the source of heat and iron-oxide is always present and usually in large amounts; silicon oxidizes before phosphorus; and the oxidation of carbon before or after phosphorus is determined by the temperature. Lack of complete control over the reactions which results from producing the requisite temperature by combustion in the furnace chamber thereby necessitating loss of iron as oxide in the phosphate slag is the very feature which electric heating can correct.

The Electric Furnace has been found well adapted to removing phosphorus by oxidation in the old way, but not commercially, and on careful consideration it is difficult to see how it could do so commercially in competition with the Open Hearth. The process of removal of phosphorus in the Heroult Furnace, for example, as practiced by the United States Steel Corporation, has been to charge blown steel into the furnace and melt on top of it a slag of lime and iron oxide. The reactions are identical with those in a basic open hearth. And in spite of the fact that the temperature can be maintained high, the removal of phosphorus in a large furnace takes anywhere from 20 minutes to an hour and a half, according to the amount of phosphorus removed. After the phosphorus is separated in a slag high in oxide of iron, that slag has to be removed in order that the bad effects of the oxides contained therein on the steel may be remedied. It is certainly difficult to see wherein lies the advantage of using costly electrical energy, electrodes, etc., to do the same thing that is done with cheaper fuel heating in a basic open hearth. And this is gradually becoming realized. After removing this first slag, it is replaced by a reducing slag to remove the oxygen from the metal. Here metallurgists have gone to the other extreme; they have aimed at and obtained the strongest reducing conditions possible by use of solid carbon and high temperatures. They have used as a measure of the intensity of such reducing conditions the formation of carbide in the slag. And these conditions are such as will readily reduce phosphorus compounds in the slag.

One method of avoiding two slags was proposed and tried out. It consisted in the use of a solid reducing agent, such as fine coke, added to the oxidizing slag after the phosphorus had been taken up by that slag. The object of this was to reduce the iron-oxide of the slag and leave the phosphorus as calcium phosphide. The results of the tests on this process indicated that the use of a solid reducing agent at the elevated temperatures necessary in a steel furnace not only reduce the iron, but also the phosphorus and the latter goes back into the metal. No other result could have been expected. The explanation of the above reaction is simply that solid carbon has a stronger affinity for oxygen than has phosphorus at the temperature of molten steel in an electric furnace, even though the phosphorus be combined with lime as calcium phosphate. In other words, the reducing conditions acting on the slag are so strongly reducing that phosphorus goes back into the metal.

High phosphorus iron-ore has been partially reduced in the presence of lime without practically any of the phosphorus entering the metal, the phosphorus being retained in a slag very high in oxide of iron. Such reduction of iron and separation from phosphorus has been carried out in an electric furnace by using insufficient carbon to completely reduce the ore, since solid carbon, if present, will, of course, reduce the calcium and iron phosphates at the elevated temperature maintained. The action here of solid carbon is similar to that in a blast furnace where the presence of an excess of solid carbon causes reduction of oxide of phosphorus and it is found in the metal. In an electric ore reduction furnace, even with a basic lining, excess of coke will produce the same result and the presence of lime does not overcome this effect. On the other hand in an electric reduction furnace, when the carbon reducing agent is limited, the phosphorus does exactly what it does in an open hearth—slags with iron-oxide as iron phosphate and combines with lime to form calcium phosphate after the carbon is used up by combination with oxygen of the ore. The above facts show why it is not possible to reduce iron from the first slag in the Heroult steel refining furnace by use of coke without reducing phosphorus back into the metal.

It is a fact that at an elevated temperature, oxide of iron is more easily reduced than calcium-phosphate and it is evident that if the proper intensity of reducing conditions be maintained at the elevated temperature, oxide of iron may be completely reduced without reduction of calcium phosphate. Such conditions are obtainable by use of a gaseous reducing agent such as ordinary producer gas meanwhile maintaining the temperature electrically.

The various reactions of phosphorus associated with iron may be summarized as follows:—

1. At temperatures under 1450°C., phosphorus in pig iron has greater affinity for oxygen than has the carbon in the pig iron, but less affinity for oxygen than solid carbon in the presence of pig iron.
2. At temperatures above 1450°C., the affinity for oxygen of the carbon dissolved in iron becomes greater than the affinity of phosphorus in the iron and the dissolved carbon can reduce calcium phosphate in the slag as, of course, solid carbon can do also.
3. Phosphorus oxidizes in presence of lime and iron-oxide to calcium phosphate in absence of silicon or solid carbon.
4. Silicon reduces calcium phosphate nearly always, but there may be a range of temperature under 1450° where phosphorus oxidizes to calcium phosphate more easily than silicon to calcium silicate.
5. Solid carbon will reduce calcium phosphate contained in a slag or bath of iron and phosphorus will go into metal.
6. Calcium phosphate can form without oxidation of iron in presence of carbon dissolved in pig iron at low temperature.
7. Calcium phosphate can form without oxidation of iron in absence of carbon and silicon at high temperatures; *i. e.*, above 1450°C.
8. Oxide of iron can be reduced without reduction of calcium phosphate contained in same slag.
9. Solid carbon is a stronger reducing agent than carbon dissolved in the iron probably because of the affinity of the metal for Carbon.

It is apparent that in all of the present processes, the complete control of at least one important factor is either lacking or has not been utilized. In the open hearth process, it is the control of the reducing conditions that is limited and likewise in the Bessemer process; but in this latter process, the control is further limited by the necessity of raising the temperature by oxidation of elements in the charge itself. In the electric furnace, however, where heat can be produced independently of combustion or chemical reaction, this important factor—namely, intensity of reducing conditions—can be controlled at will and with ease. Up to the present time, this fact appears not to have been appreciated by metallurgists, judging by present methods. It is in the complete control of the reducing conditions that important possiblities of Electric Heating lie, and as this fact becomes more generally recognized and used it is probable that some method will be devised for measuring the intensity of reducing conditions or equilibrium conditions. Since the intensity of reducing conditions is the reverse of the intensity of the oxidizing conditions, the term "oxygen pressure" may find a use as a measure of them.

Among the reactions made possible by control of the reducing conditions and temperature simultaneously is the reduction of oxide of iron from a slag containing calcium phosphate without reduction of the phosphorus contained therein. Naturally the origin of the phosphorus containing slag or charge is immaterial; it may be raw ore containing phosphorus, or it may be a slag in which some of the original oxide of iron served to provide the oxygen for combination with phosphorus, the oxide of phosphorus subsequently combining with lime to form phosphate. Or the reducing conditions may be so controlling as merely to prevent oxidation of iron which, at the same time, causes phosphorus to oxidize and combine with lime.

In the writer's experiments along this line, it has been found that at temperatures below about 1400°, the phosphorus was easier to oxidize than carbon from pig iron. And it was found that the phosphorus could be oxidized in the presence of lime without any resultant oxidation of iron and with practically no oxidation of carbon; that phosphorus could be oxidized in the presence of lime without oxidation of manganese; and a very interesting further observation was made—namely, that at certain temperatures between the melting point of pig iron and about 1350°C., phosphorus oxidized in certain cases in the presence of lime without any appreciable oxidation of silicon. This would indicate a reversal of oxygen affinity of these elements—phosphorus and silicon in pig iron in the presence of lime.

A fusible slag results from proper proportions of acid and basic radicals. It has been found that the silica content in the slag may be as high as 30% without apparently hindering the removal of phosphorus. Phosphorus was separated in slags containing this much silica and yet practically no iron oxide was present in that slag. This points to the possibility of a low melting point slag for holding phosphorus.

The reduction of oxide of iron from a charge or slag containing phosphorus as calcium phosphate without reduction of the latter requires essentially the same control of the conditions as does the selective oxidation of phosphorus in presence of lime forming calcium phosphate, without oxidation of iron. Electric heating is the only practical way of accomplishing such control.

It is not to be doubted that metallurgists will very soon appreciate the distinction between various degrees of oxidation and reduction, where they have not already done so, since in so many cases undesired elements can be separated from metals by oxidation of the impurity and reduction of the metal. When this becomes generally appreciated it is prophecied that Electric Heating will come into use to an extent that can now hardly be thought possible.

SUR LES CREUSETS DES FOURS À PLOMB

J. P. Doanides
Laurium, France

C' est deux cas de mon experience comme chimiste metallurgiste, directeur de la Societé des Usines du Laurium, que je viens communiquer aux specialistes.

I

Les fours à plomb de la Societé des Usines du Laurium sont installés tout près de la mer et à la côte+ 0, 80m. Il est arrivé l' année derniere que le creuset d'un d' entre eux, à la suite d' une marche trés intensive, et d' une allure très chaude, fut rongé par le speiss à un point inquietant. En sondant par le trou de la coulée nous constations une profondeur de 0,40m inferieure à la normale. Nous risquions donc d' avoir par les infiltrations du metal fondu à travers la maçonnerie ainsi deteriorée, d' avoir en contact les matiéres fondues du creuset avec l'eau de la mer, qui arrive jusque aux fondations des fours.

J' ai remedié à cet état des choses en alimentant mon four avec une forte proportion de mattes sulfureuses (20%) d' une teneur de 23% de S et 7% de Pb. Le resultat en a été très satisfaisant Après quelques jours d' irregularité, la marche du four devint normale et son rendement identique à celui des autres.

Je suis parti du fait accusé par tous les metallurgistes par leur experience, que les mattes engorgent les creusets et diminuent leurs dimensions, surtout en profondeur.

II

Pendant un arrêt pour reparations d'un Water Jacket de 0,90/2,20 m alors en marche à l' usine de la même Societé, je me suis rendu compte que la maçonnerie du creuset était fissurée jusque aux fondations, son armature metallique était craquée, et qu' il y avait fuite de plomb fondu, dont le creuset était plein.

J' ai été obligé de vider le creuset et ne pouvant pas proceder à la reparation necessaire, lorsque aprés deux jours j' ai remis le four en marche, je n' ai pas osé remplir le creuset avec du plomb comme de rigueur, craignant de nouvelles fuites. Par contre j' ai cherché le moyen de les empecher, en fermant les fissures par une matiere moins fluide que le plomb fondu.

Je l' ai trouvé en une scorie tres fluide de 28.00% de SiO_2–26.00% de Fe–8.00% de Mn–4.00% de CaO–et 3.50% d' Al_2O_3. Ayant donc fait un bon feu, j' ai rempli le four avec la charge appropriée, et j' ai donné le vent en pression. Le creuset de cette façon s' est vite rempli completement de scorie, qui par la pression de la ventilation a été introduite dans les fissures du fond. Peu apres les charges plombeuses ont donné leur metal. La marche fut établie normale comme au paravant.

Abstract

ON THE CONSTITUTION AND GENESIS OF CERTAIN LIGNITES AND SUB-BITUMINOUS COALS

REINHARDT THIESSEN
Bureau of Mines, Washington, D. C.

Coals are composed chiefly of a residue of the most resistant components of plants, of which resins, resin-waxes, and higher fats and alcohols are the most important.

Plant substances differ very markedly in their resistance to various agencies. Those substances involved in the life and the support of the plant are relatively labile, whereas those involved in some protection function, or are to be looked upon as waste products, are relatively stable. Of these substances like the resins, waxes, resin-waxes, higher fats and alcohols are the most stable.

After the *death* of the plant there begins, governed by various conditions imposed upon the deposit, a partial decomposition, maceration, elimination and chemical reduction, brought about chiefly by the agencies of organisms, fungi first, followed closely by bacteria. The least resistant components are removed first, leaving the more and the most resistant behind in a residue called peat.

The process of elimination and chemical reduction begun in the peats, chiefly by biochemical means, is taken up and continued by dynamochemical means into and through the various grades of coals.

Lignites and sub-bituminous coals are therefore composed of a residue or debris consisting of the more and the most resistant plant substances in a macerated and changed condition, in which are usually embedded logs, stems, branches, or fragments thereof also in a much changed condition, in varying proportions.

The "wood" has been reduced very much, and since its resin

contents have suffered little if any change, it has become very resinous.

The debris is composed (a) of cellulosic substances in a greatly altered condition, in the shape of fragments of tissue, small complex of cells, single cells and fragments of cells; (b) resinous substances; (c) cuticles; (d) spore-exines; (e) pollen-exines; and (f) a variety of a small number of other unimportant bodies. The interstices of these bodies are in turn filled in with a still finer originally macerated matrix consisting essentially of the same substances, either in a very high state of comminution or the residue of them. This component is termed the ground- or binding-mass.

Highly macerated leaf cuticles are an important component of the ground mass.

The proportion, or distribution, of the various bodies named, varies considerably in different beds and in different layers of the same beds.

The ratio of the cellulosic components to the resinous and cuticular components varies, generally, inversely to the state of maceration and the degree of metamorphism of the coal.

ELECTRIC INDUCTION AND RESISTANCE FURNACES FOR STEEL

C. H. VON BAUR

Electric steel furnaces of the induction type have been in operation for over a decade, using single-phase current. Lately, furnaces of improved design have been operated directly from two-phase and also from three-phase current, without any previous transformation into the simpler single-phase.

I wish to lay before you a few recently determined facts concerning the action of the rotating field which is present in polyphase induction furnaces.

This rotating field is the short-circuited secondary, or the molten metal; and in the two-ton size Roechling-Rodenhauser furnace this rotating field of molten metal wore out the lining too rapidly at certain places in the hearth. Oddly enough, when this same style of furnace was made a little larger, in a three-ton size, the rotating field did not manifest itself sufficiently to have any deleterious effect on the lining, owing no doubt to the widening of the hearth. The lining lasts as long in this case as in a single-phase furnace of equal size, for as many as four to five hundred heats have been taken from one lining when using hot charges, and about half as many heats when charging cold material. In order, however, to simplify the polyphase furnace hearth, and consequently lengthen the durability of the lining, it was deemed best to construct the furnace on the two-phase principle. This furnace construction has two transformer cores protruding through the bath, instead of three, as with the three-phase furnace. This two-phase construction employs the well known figure-eight hearth, which in additon to being simpler from both an electrical and metallurgical standpoint, is also more efficient thermally, as the radiation losses are less. Metallurgically, the furnace is better and easier to operate, as the hearth is wider and shorter compared to the corresponding single-phase size having the same shaped hearth. This makes the rabbling-off of slag easier than with the single-phase furnace, and compared with the three-phase style furnace this rabbling is also more convenient, as the slag is removed from doors which are in a straight line with the spout.

This two-phase type of construction is also more simple compared to the three-phase type, as only two coils are wound about the transformer cores instead of three. When three-phase current must be used it is transformed in the furnace itself to two-phase, without employing auxiliary transformers having the well known Scott connection. The heat regulation of the furnace is then accomplished by regulating the three-phase incoming current by means of a simple and inexpensive three-phase induction regulator. This improvement will also decrease the installation cost. I am glad to say that all Roechling-Rodenhauser and improved-type induction furnaces will be built in this form.

I now wish to lay before you a new metallurgical fact concerning steel at a very high temperature, such as has been attained in the induction furnace. It is a high-temperature phenomenon which might be called a new critical point of iron.

A test was carried on in an eight-ton induction furnace having enough electrical power behind it for a fifteen-ton furnace, of this type. The full capacity of the alternator was used for the test, and, as there was power to spare, the charge was greatly overheated. In fact, the temperature obtained was so high that the magnesite lining was completely fused even below the slag line, which indicates that the temperature must have been at least 2400° to 2600°C.

Common steel, as is well known, has a critical point at a temperature of about 760°C., and when arriving at this point it seemingly does not rise in temperature so rapidly, whereas when the temperature reaches about 810°C., a sudden and rapid rise in the temperature of the steel takes place. The same thing seems to be repeated at the higher temperature alluded to and another critical point seems to be reached. The metallurgists present at this test stated that when a temperature of about 2350°C. was obtained, the steel became thick and viscous. However, after the temperature had risen some 200° higher, it again became liquid and was then poured into the ladle. There it was naturally cooled down somewhat, and became again thick and viscous to such an extent that it was impossible to empty the ladle into the ingot moulds. A heavy rod of cold steel, about eight feet long, and two inches in diameter, was then put into the ladle, by means of which the steel was cooled down below the critical point, whereupon it suddenly became as liquid as water and could be easily emptied into the moulds. The ordinary tests showed that the steel was of the usual good quality, but no other tests were made on it to determine whether or not this extraordinary heating had had any other effect upon the metal.

I regret to say, that the latest developments and improvements made in induction furnaces this year in Germany, which I expected to lay before the Congress at this time, have been delayed in reaching me, but in closing I may add that the Roechling-Rodenhauser Induction Furnaces and their improved types will shortly be built in sixteen and twenty ton sizes, both here and abroad.

THE USE OF THE BALLISTIC MORTAR FOR DETERMINING THE STRENGTH OF EXPLOSIVES

Arthur M. Comey and Fletcher B. Holmes
Chester, Pa.

While frequent use has been made of the Druckmesser and Trauzl Tests in the experimental work carried on at the Eastern Laboratory, the Ballistic Pendulum or Mortar test has usually been preferred for the determination of the strength of explosives, for the reasons given in another paper presented to this Congress. In this paper we will describe the test as made at the Eastern Laboratory, and will point out certain precautions which must be taken to insure accuracy. The test is not new but it appears that it has not been widely used in recent years. The mortar itself weighs about 475 pounds, and is carried by means of two steel rods about 10 feet long, which are supported at the top by knife edges to allow the mortar to swing freely. Sketches 1 and 2 show the dimensions of the mortar and shot. The shot "C" is perforated in the line of its axis by a hole "D," just large enough to take a fuse. The explosive to be tested is weighed out into 10 gram lots, each of which is wrapped in tin foil with a cap and fuse. Before a charge is placed in the mortar, the fuse is run through the axial perforation in such a way that when the shot is slipped into the explosion chamber "A" of the mortar, the explosive is in the chamber "B."

The end of the fuse projects beyond the outer end of the shot to make it possible to light it after the shot is in position. The detonation of the explosive throws the shot against a suitable barricade, and produces also a recoil of the mortar, the amount of which is proportional to the strength of the explosive. The recoil is not sensibly affected by variations in quickness, such as are encountered in high explosives, but appears to depend entirely upon the pressure exerted by the products of decomposition at the moment of explosion.

It is to be expected from the design of the mortar and shot that both the shot and the walls of the explosion chamber will gradually be eroded by the hot gases, and this is found to be the case. As this erosion goes on, the recoil of the mortar for a given charge of explosive naturally becomes less. A new mortar and shot always give higher results, which gradually fall off from month to month as the mortar is used. The amount of decrease due to this cause will depend upon how much the mortar is used. We have noted a decrease with Monobel from 22.60° with a new mortar and a tightly fitting shot to 20.70° after five months' use, corresponding to a decrease of about 0.4° per month. It should be understood that this gradual decrease in recoil does not affect the accuracy of the test for determining comparative strength values, but it is evident that a test on an explosive whose strength is to be determined must always be accompanied by a parallel test on an explosive whose strength is known.

When this test was first used, there was considerable difficulty in obtaining duplicate determinations on the same explosive which would agree. A series of five or six shots made one day sometimes differed by as much as a degree from shots made on the same explosive the previous day. There were several reasons for such differences. It was formerly the custom to lubricate the walls of the explosion chamber with glycerine before each shot. It was later shown that if no glycerine were used, and the test were made with both shot and explosion chamber dry, the recoil was considerably less. It was also found that when lubrication was used, the amount of recoil was affected by the kind of lubricant employed. If water was used the recoil was increased somewhat, though not as much as with glycerine. It appeared that the action of the liquid was to prevent to a certain extent the escape of gases around the shot, and that the viscosity of the liquid used had a marked effect upon the recoil obtained. Any change in strength of the lubricant used, due either to dilution or to variation in temperature, would accordingly cause inaccuracy of the test. For this reason, the practice of using a lubricant was discontinued, and shots are always made now with the walls of the explosion chamber and the shot perfectly dry.

It was also found that it was very difficult in many cases to clean the explosion chamber thoroughly after each shot. In some cases, the solid residue from the explosive would collect in hard masses at the rear of the explosion chamber, and make it difficult to push the shot back against the shoulder. Experiments on the effect of not seating the shot properly demonstrated that if the shot failed to reach the shoulder even by a very small fraction of an inch, the recoil of the mortar was noticeably lower than it should be. Even with the explosion chamber and shot cleaned as thoroughly as could be done by careful scraping with a knife and thorough washing and drying, results were still irregular. The discovery was then made that the recoil produced by a given explosive was affected to a marked extent by the character of the explosive which had been tested just previously in the mortar. For example, the coal mine explosive, Carbonite, shot directly after a series of tests with blasting gelatine, gave a recoil of 16.66°. When a series of Carbonite shots were made, the recoil gradually decreased until it averaged only 15.56°. Furthermore, when blasting gelatine was tested directly after Carbonite, the values obtained were also decidedly lower than those obtained after a number of previous shots with blasting gelatine.

Table I below gives the Mortar recoils obtained in thirteen tests on Carbonite. These tests came directly after a series of tests on blasting gelatine.

Table I

Mortar recoils obtained with Carbonite

16.65°
15.90
16.15
15.80
15.75
15.70
15.60
15.40
15.30
15.60
15.70
15.50
15.70

The first shot, made directly after those on blasting gelatine, is high (16.65°), the next four shots average 15.90, while the average of the last eight shots is 15.56°, a drop of 1.10° from the highest.

Table II gives the results obtained in a test in the same powder, in which each shot of 10 grams of Carbonite was preceded by five shots of blasting gelatine. Only 5 grams of blasting gelatine were used in each shot. The tests were made in the order A–1, A–2, A–3, A–4, A–5, Carbonite, B–1, B–2, B–3, B–4, B–5, Carbonite, C–1, etc. Each blasting gelatine test recorded in column 1 was accordingly preceded by a test on Carbonite, while each test in column 5 was preceded by four tests on blasting gelatine.

Table II

Series	Blasting Gelatine					Carbonite
	1	2	3	4	5	
A	16.70	16.95	16.95	16.70	16.75	16.80
B	16.35	16.70	16.65	16.80	16.65	16.75
C	16.70	16.70	16.65	16.85	16.75	16.55
D	16.60	16.65	16.70	16.90	16.75	16.60
E	16.40	16.85	16.65	16.65	16.75	16.75
F	16.40	16.70	17.00	16.70	16.85	16.60
G	16.50	16.60	16.60	16.80	16.85	16.50
H	16.40	16.50	16.60	16.70	16.95	16.65
I	16.60	16.75	16.85	16.60	16.80	16.75
J	16.55	16.75	16.80	16.85	16.85	16.70
Average	16.52	16.71	16.74	16.75	16.79	16.66

It will be seen, first, that the Carbonite tests recorded in Table II average as high as the highest test in Table I, and 1.10° higher than the average of the last 8 shots in that table, and second, that the blasting gelatine tests average lowest when they are directly preceded by Carbonite tests, and highest when they follow the greatest number of tests on blasting gelatine.

Several hundred tests were made along these lines on different grades of dynamite and gelatine, to determine whether all grades gave results like those obtained with Carbonite. As a result of these tests it was found:

1. That nearly all explosives give high Mortar recoils just after the Mortar has been used for blasting gelatine, and low and rather irregular recoils when the tests follow shots with explosives other than blasting gelatine.

2. That the low-grade nitroglycerine dynamites exhibit this behavior to a greater extent than the high-grade dynamites, and furthermore that explosives with a high deficiency of oxygen, like Carbonate, are more affected than those which are evenly balanced in oxygen.

It seemed from this that those explosives which left the largest amount of solid residue in the Mortar were the ones which had the greatest effect on tests made afterwards. The residue left in the explosion chamber was quite noticeable, and was appreciably greater in the low-grade explosives, and in those which had a high oxygen deficiency. Blasting gelatine, on the other hand, as would be expected, left practically no residue. It therefore appeared that the decrease in recoil in these cases was due to the effect of the solid residue left by the explosive tested just previously, and that the high recoils obtained just after blasting gelatine had been tested, were due to the facts, (1) that blasting gelatine leaves no residue, and (2) that the blasting gelatine tests clean out the walls of the explosion chamber more effectively than can be done by mechanical means. To confirm this assumption, a long series of tests were made on Monobel, which also should leave very little residue. In this case there was no decrease in recoil with succeeding shots, and the results at the end of the series were fully as high as those at the beginning. This effect of the residue from one test, on the recoil produced in succeeding tests, was undoubtedly responsible to a great extent for the irregular results formerly obtained with the Ballistic Mortar.

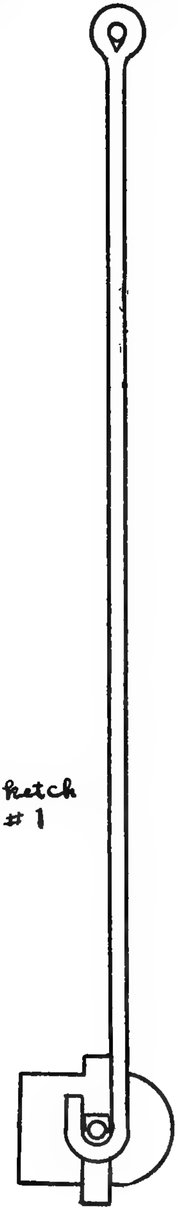
It appeared that it should be possible to obtain uniform results by firing enough shots of blasting gelatine before every shot with the explosive which is being tested to thoroughly clean the explosion chamber of all residues from previous shots, thus always leaving the bore in the same condition. It was found that this could be accomplished by making two shots of blasting gelatine before every shot of the explosive being tested. This practice has accordingly been adopted.

The present procedure in making the test is therefore as follows: If an explosive is to be compared with a standard 40 % dynamite, 10 samples of the explosive of 10 grams each are wrapped in tinfoil, with a cap and fuse, also 10 samples of the same weight of standard 40% dynamite. A number of blasting gelatine shots are also prepared. These are not weighed, but consist of a small piece of blasting gelatine weighing approximately 5 grams. In making the test, two shots of blasting gelatine are first made without measuring the recoil. A shot of the explosive whose strength is being determined is then made, and the recoil measured. This is followed by two blasting gelatine shots, then by a shot with standard 40% dynamite. Then two blasting gelatine shots are made, another shot of the explosive which is being tested, etc.

Tested in this way, explosives which are nearly evenly balanced in oxygen, or which have a slight deficiency of oxygen, give results which check rather more closely than explosives which have more than enough oxygen for complete combustion. In the former case, the extreme variation among 10 successive tests on the same explosive will be from 0.15° to 0.30°, while in the latter case it may at times run as high as 0.4° or occasionally even 0.5°. As we have shown in another paper presented to the Congress, this variation is less than that usually obtained in the Trauzl test, and is much less than that given by the Druckmesser test.

On account of the erosion of the shot and of the walls of the explosion chamber, the recoil given by any explosive gradually decreases from month to month as the Mortar is used. It is necessary to bear this fact in mind if accurate conclusions are to be drawn from the Mortar tests. To avoid errors which might arise from the use of values previously obtained for standard explosives, it is our custom always to test the standard at the same time that an explosive of unknown strength is being tested. We have ordinarily used as standards the various grades of nitroglycerine dynamite, since it is convenient to express the strength of a new explosive in terms of these well known grades. It is also possible to use a single standard explosive and to determine the relative strengths of this explosive and the explosive which is being tested. We find trinitrotoluol a convenient explosive for this purpose. The method is to test 10 grams of the explosive whose strength is being determined against different weights of trinitrotoluol until a weight of the latter is found which gives the same recoil as 10 grams of the former. If this weight is 7.5 grams, the new explosive is 0.75 as strong as trinitrotoluol.

The Ballistic Mortar is in constant use at the Eastern Laboratory, averaging possibly a hundred tests a day. Used carefully, with the precautions described above, we find it by far the most satisfactory of the tests proposed for the determination of the strength of explosives.



Sketch
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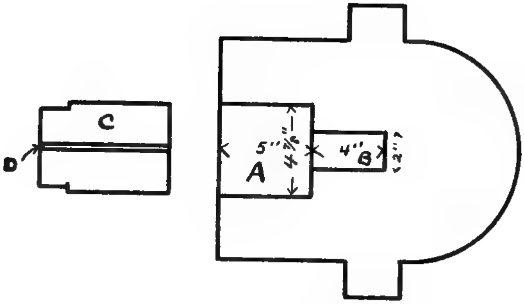


Sketch # 2

METHODS FOR THE DETERMINATION OF THE EFFECTIVE STRENGTH OF HIGH EXPLOSIVES

Arthur M. Coney and Fletcher B. Holmes
Chester, Pa.

The question of the determination of the effective strength of high explosives is more important now than it has been at any time in the past, because of the many different kinds and grades of explosives now on the market. In America the multiplication of grades has probably gone on even more rapidly than in Europe. One company sells at the present time about one hundred and twenty-five different grades of dynamite, each of which offers a particular combination of physical and chemical properties which adapts it, more than any other grade, to a particular kind of work. The proper grading of these dynamites requires a careful study of the tests available for the purpose.

The power of an explosive to move rock depends on two facts: first, that a very small volume of the solid or liquid explosive forms a very large volume of gas, and second, that this change from a small to a large volume takes place in an exceedingly short interval of time. Explosives differ both in the volume of gas formed when detonation takes place, and in the time required for the change from the solid or liquid to the gaseous state, and both factors have their effect on the power of the explosive to move rock. For this reason it has been held by some that the best test to determine the power of an explosive is one the results of which are affected by both these factors, since a test of this kind will present conditions which approach those which obtain in the actual use of the explosive. But the difficulty is that while a test of this kind may subject the explosive to conditions which are more or less like those which would be found in one type of work, another work which the explosive will be required to do may be entirely different. For example, when rocks too large to handle are thrown out in a blast, it is the custom in some quarries to break them up by means of a few sticks of dynamite simply laid on top of the rock and covered with a shovelful of mud. It is perfectly evident that no explosive will do this work, however large a volume of gas it generates, unless it is at the same time very quick. For heaving out coal, on the other hand, where it is desired to bring it out in large lumps, with the explosive strongly confined in a borehole, a very slow dynamite is required, and one which is very quick is not at all satisfactory. With a test which is affected both by the volume of gas formed at the moment of detonation and by the quickness with which the explosive reaction takes place, it is impossible to judge how much of the effect is due to one factor and how much to the other. Admitting that the fitness of a given explosive for any given work depends upon the combined qualities of strength (used here in the sense of the pressure generated in a given volume by a given amount of explosive at the moment of detonation) and quickness, it must be agreed that a test which is affected by variations in both strength and quickness is of little value in judging an explosive of unknown power, but that the most valuable tests are those which show, as nearly as possible, only one quality, i. e., either strength alone or quickness alone.

The earliest test for quickness used at the Eastern Laboratory was the well known lead block compression test. In this test as first applied at the Laboratory, two lead cylinders 1½″ in diameter by 1¼″ high were set one upon the other on a steel plate. The upper cylinder was capped by a steel disk of the same diameter and ¼″ thick. On this steel disk were placed 100 grams of the dynamite to be tested, contained in a paper shell of the same diameter as the lead cylinder, and the dynamite was fired by means of a cap and fuse without other confinement than that offered by the paper shell. In recent tests we have used a single lead block 1½″ in diameter by 2½″ high, instead of two blocks each 1½″ x 1¼″ high.

It is of course apparent that, theoretically, this test cannot be entirely unaffected by the strength of the explosive. Practically, however, we have found that the strength of the explosive is of little moment in determining the amount of compression of the lead cylinder under the conditions of the test. The compression appears to depend almost entirely upon the quickness of the explosive. This is well illustrated by the behavior of certain gelatine dynamites in the test. Gelatine dynamite is made in grades from 35% to 80% strength. These gelatine powders contain, besides the gelatinized nitroglycerine, mainly sodium nitrate and wood pulp. They increase regularly in strength with increasing nitroglycerine content, as can be shown by any of the tests ordinarily used for determining the strength of explosives. All of them, however, from the lowest to highest grade, give practically identical lead block tests. This fact in itself is sufficient to show conclusively that the lead block compression test shows the quickness of an explosive alone and is not noticeably affected by the strength of the explosive. The lead block tests on these powders have been confirmed by actual determinations of velocity of detonation, and it has been found that they all have practically the same velocity. Even blasting gelatine, which is immensely stronger than the low grade gelatine powders mentioned above, will sometimes give a lead block compression no greater than that given by the latter, and in such cases a velocity of detonation test will show that the blasting gelatine has a low velocity.

We found another illustration of the significance of the lead block compression test with nitroglycerine. Several years ago, before we were equipped to make velocity of detonation determinations, we made a series of lead block tests on nitroglycerine using detonators containing 0.8 gram of 90–10 fulminate-chlorate mixture, and obtained very erratic results. In some shots, the blocks were broken to pieces, while at other times they were only very slightly compressed. With larger caps, even up to 3 grams of fulminate, the results were much the same, indicating either that the test was unreliable or that nitroglycerine was erratic in its detonation. When the Bichel apparatus for the determination of velocity of detonation was installed, results were obtained which confirmed the lead block compression tests, as shown in the table below.

TABLE I

Velocity of Detonation of Nitroglycerine Determined in Tubes 10 Feet Long by the Bichel Method

Weight of Detonator Charge	Diameter of Tube Containing Nitroglycerine	Velocity of Detonation Meters per Second
0.8 gram	$1\frac{1}{2}$ inches	2412 1627 3846 2293
1.5 grams	1 inch	1539 6783 7877 1463 8410
1.5 grams	$1\frac{1}{2}$ inches	8527 1288

The low velocities (1288 to 2412) correspond to the poor lead block compression tests, and the high velocities (6783 to 8527) to the tests in which the blocks were strongly compressed and broken.

It was later found that good lead block tests could always be obtained if the nitroglycerine was detonated by a special detonator, much more powerful than any of those previously used. When velocity tests were made by the Bichel method, detonating the nitroglycerine by means of the special detonator, results were obtained as follows:—

Shot No. 1	7129 meters per second
Shot No. 2	7603 meters per second
Shot No. 3	6675 meters per second
Shot No. 4	7528 meters per second

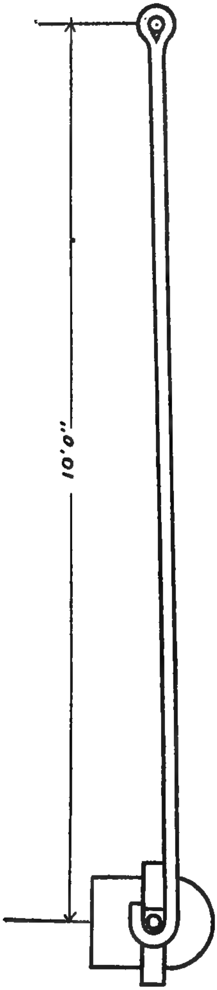
There is no question that for a simple and approximate test for the quickness of an explosive, the lead block test is useful. There is one fact, however, which must not be overlooked, and that is that when dynamite is detonated by means of a cap the detonation does not always start at the rate which it finally attains. Many cases have been found in which the first few inches of a column of explosive detonate with a low velocity, the velocity gradually increasing until it reaches a maximum after a certain length of column has detonated. In a case like this, the lead block test will give an indication of the rate at which the explosive detonates through the first inch or two of the column, but gives no clue as to the velocity which will be attained in a longer column. This fact deprives the test of much of the value which it would otherwise have.

The lead block test is not at present so essential as it was some years ago, since we now have methods by which we can measure directly the velocity of detonation of an explosive, either by the method of Bichel, or by the newer and in many respects more convenient method of Dautriche. Both of these methods we have found quite accurate and exceedingly useful. With explosives which have a velocity of detonation very much higher than that of the detonating fuse, the Dautriche test is apt to give erratic results, some records being obtained which indicate for the explosive which is being tested a velocity which is probably much higher than the truth. We have found that when testing explosives of this kind, it is entirely possible that the detonating wave may jump through the air from the explosive to the fuse, reaching the latter at a point some distance from the cap, and thereby causing erratic results. Results of this kind have been obtained with explosives having a velocity of 7000 or more meters per second. With explosives of lower velocity, no such difficulties are encountered, and very concordant and satisfactory results are obtained. Since there are very few explosives in common use which have a velocity of detonation much higher than that of the detonating fuse, the question of the jumping of the detonating wave through space is not very serious, and does not detract greatly from the value of the test.

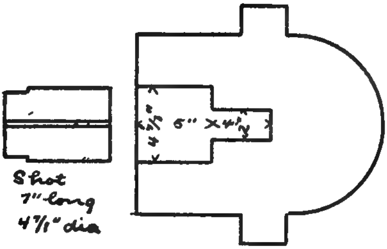
For the determination of strength, several different tests have been proposed and used. The old mortar test was carried out by throwing a shot from a stationary steel mortar, set at an angle of 45°, using a fixed amount of dynamite, and measuring the distance to which the shot was thrown. Another test is the Trauzl Block Test, which is used much more on the Continent than in America. The Druckmesser Test, more recently developed by Dr. Bichel, is used in several places in Europe and in at least two places in the United States—at the Government Testing Station at Pittsburgh, and at the Eastern Laboratory of the E. I. du Pont de Nemours Powder Company. These tests are so well known that we do not need to describe them here. Another test which has been much used at the Eastern Laboratory is the Ballistic Pendulum Test. This test employs a steel mortar weighing about 450 pounds, with a bore 4⅞″ in diameter and 5″ deep, and a chamber behind 2″ in diameter by 4″ deep. A cylindrical shot weighing about 36 pounds fits the mortar closely, and has a hold running lengthwise through its center just large enough to admit a fuse. Ten grams of dynamite are used in the test. The shot is projected against a suitable barricade and the recoil of the mortar is measured by an indicator on the arc of the circle, and is taken as a measure of the strength of the dynamite. The form and dimensions of the mortar and shot are shown in the accompanying Sketch I.

The only one of the above tests which gives results which can be translated directly into actual pressures is the Druckmesser Test, and for this reason the equipment for the latter test is essential to a laboratory devoted to the examination of explosives. For constant routine tests, however, it is not necessary that actual pressure figures be obtained each time; it is sufficient to compare the explosive in question with well known standards, and for this purpose it is possible to use a test which is less cumbersome than the Druckmesser Test, and which can be carried out in much shorter time. By means of the standard, which has already been tested in the Druckmesser, results of other comparative tests can always be translated into pressures, if so desired.

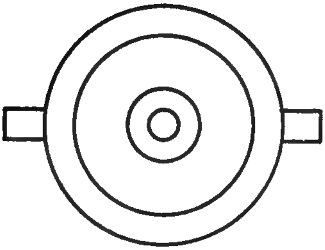
In America all dynamites contain active dopes. The so-called "straight" dynamites consist essentially of nitroglycerine absorbed in a mixture of sodium nitrate and wood pulp in such pro-



General View



Longitudinal Section



Front Elevation

portions as to contain just about enough oxygen for complete combustion. These grades vary in nitroglycerine content from 75% to 20%, and even lower. Gelatine dynamites, low-freezing dynamites, etc., are similarly graded from strong to weak. In using tests which give comparative but not absolute results, we shoot a known standard alternately with the explosive which is being tested. As the standard we may use blasting gelatine, or trinitrotoluol, determining the number of grams of the standard equivalent to 10 grams of the explosive, or we may use the standard nitroglycerine grades, determining what grade is nearest equivalent to the exlposive which is being tested.

To be of greatest value for practical purposes, a test for strength must conform to three requirements:—

1. It must give uniform and exact results.
2. It must give a measure of strength without being affected by any other quality of the explosive.
3. It is of advantage to have a test which can be operated as expeditiously as may be, and at small expense.

The extent to which uniform results can be obtained from the Druckmesser, Trauzl, and Ballistic Mortar Tests may be illustrated by the following Tables Nos. II, III, and IV. The figures given in these tables are taken from actual determinations made at the Eastern Laboratory, and are representative of the kind of results which we are able to obtain in using the tests.

The Druckmesser results in Table II are not very satisfactory. It will be seen that in many cases the pressures obtained in the 15 liter chamber with small cooling surface were lower than those obtained in a chamber of the same volume with larger cooling surface. Various methods were used for determining the pressures from the indicator curves obtained, from extending the top line from the point where it becomes straight back to the origin of the curve, to a mathematical calculation of the position the top line would occupy at its highest point, based on the position of succeeding lines. Results obtained by the different methods varied somewhat, but not nearly enough to account in any way for the differences shown in Table II. There have been a number of other cases where the amount of cooling surface has

TABLE II

Druckmesser Tests on Trinitrotoluol

Volume of Chamber=15 liters. Three Different Surfaces

Test Number		1			2			3			4	
Grams Trinitrotoluol Shot		100			250			100			100	
Cooling Surface	Small	Medium	Large	Small	Medium	Large	Small	Medium	Large	Small	Medium	Large
Pressures Obtained in 15 Liter Chamber Kg. per sq. cm.	37.3 34.9 38.0 39.0	35.0 36.6 37.7	40.2 38.6 38.4	95.7 99.1 98.8 103.2 107.1	103.4 100.1 100.9 103.4	101.6 91.6 100.0 100.6	36.3 35.0 35.5	37.0 38.7 35.2	35.2 32.3 33.8	35.8 34.8 36.0	34.9 33.5 33.7	32.3 32.2 34.2
Average	37.3	36.4	39.1	100.8	102.0	98.5	35.6	37.0	33.8	35.5	34.0	32.9
Difference between extremes	4.1	2.7	1.8	11.4	3.3	10.0	1.3	3.5	2.9	1.2	1.4	2.0
Percentage difference based on average pressures	11.0	7.4	4.6	11.3	3.2	10.1	3.7	9.5	8.6	3.4	4.1	6.1
Pressure corrected to O surface	35.0			104.6 (41.8 per 100 grms. trinitrotoluol)			39.0			38.8		

had no apparent effect, although with most explosives the pressure diminishes quite regularly with increasing cooling surface. It is unquestionably necessary to make a large number of duplicate determinations in order to obtain reliable figures and even then the results are only approximate.

TABLE III

Trauzl Block Test

10 Grams Trinitrotoluol

Test Number	1	2	3	4	5
Expansions in cc.	243.9 249.4 241.6 241.2 247.7	251.1 255.8 251.4 255.6	245.8 249.6 251.1 255.8 251.4 255.6	243.9 244.5 243.5 243.9 241.6	246.8 245.8 252.6 253.2 254.2
Average expansions in cc.	244.8	253.5	251.5	243.5	250.5
Difference between extremes in cc.	8.2	4.7	6.2	2.9	8.4
Percentage difference, based on average expansion	3.3	1.9	2.5	1.2	3.4

TABLE IV

Ballistic Mortar Test

10 Grams Trinitrotoluol

Test Number	1	2	3	4
Mortar Recoils—Degrees	18.80 18.85 18.85 18.55 18.75 18.65 18.65 18.65	18.85 18.95 18.75 18.65 18.95 18.85 18.75 18.65	19.05 19.10 19.00 19.00 19.00 19.05 19.15 19.05	18.85 19.10 19.10 19.00 18 65 19.15 19.10 19.15
Average Recoil—Degrees	18.72	18.80	19.05	19.01
Difference between extremes—degrees	.30	.30	.15	.50
Percentage difference based on average recoil	1.6	1.6	0.8	2.6

In the Trauzl and Mortar Tests, Tables III and IV, the check between duplicate shots is better. The five series of Trauzl Tests were made on different days with blocks from different melts of lead. This accounts for the variation among the averages. The four series of mortar tests were also made on different days.

In a comparison of this kind, it cannot be assumed that because the percentage variation in one test is greater than in another the first test is necessarily less accurate than the other, without considering at the same time the relation of these variations to differences in stength which it may be desired to determine, for the reason that a given difference in strength, represented, for example, by an increase from 9 to 10 grams of blasting gelatine, may increase the results obtained in one test more than in another. A difference of this sort is possible because the results of the tests are empirical and not absolute. To illustrate this, we give in Table V the Trauzl expansions and Ballistic Mortar recoils for different weights of blasting gelatine, varying from four to seven and a half grams.

The percentage increase in Trauzl expansion with an increase of a half gram in the weight of the charge is about twice the percentage increase in Ballistic Mortar recoil, indicating that if the percentage variation between checking determinations in the Trauzl Test is twice as great as the percentage variation in the Ballistic Mortar Test, the two tests will be about equal in accuracy. Turning again to Tables III and IV, the average extreme variation in the Trauzl Test is 2.5%, against 1.6% for the Mortar Test. In these special cases, then, the two tests were of nearly equal accuracy with respect to checks between duplicate determinations.

The figures in Table VI will serve to illustrate still further the relative significance of the variations between duplicate determinations which are ordinarily encountered in the prosecution of the tests. This table gives the results of Druckmesser, Trauzl, and Mortar Tests on dynamite grades containing 10, 20, 30, 40, 50, and 60 per cent nitroglycerine, together with the relation between (1) the maximum variation among duplicate determinations in each grade and (2) the difference between that grade and the next succeeding grade.

The average extreme variation in the shots, expressed as percentages on the figures obtained in the three tests, are as follows:

Druckmesser Test....................	6.9
Trauzl Test..........................	6.4
Ballistic Mortar Test..................	1.9

TABLE V

No. of Grams Blasting Gelatine	Traual Test			Ballistic Mortar Test			Ratio, % increase in Mortar Test to % increase in Trauzl Test
	Expansion cc.	Increase in expansion for next succeeding weight	Percent increase	Recoil Degrees	Increase in recoil for next succeeding weight	Percent Increase	
4.0	158	27	17.1	14.61	1.14	7.8	.45
4.5	185	29	15.7	15.75	.96	6.1	.39
5.0	214	29	13.6	16.71	.87	5.2	.38
5.5	243	29	11.9	17.58	.95	5.4	.45
6.0	272	30	11.0	18.53	.89	4.8	.44
6.5	302	32	10.6	19.42	.88	4.5	.42
7.0	334	29	8.7	20.30	.85	4.2	.48
7.5	363			21.15			

TABLE VI

Druckmesser, Trauzl and Ballistic Mortar Tests on Dynamite Grades Containing from 20% to 60% Nitroglycerine

Percent Nitro-glycerine in Dynamite.	Druckmesser Test				Trauzl Test				Ballistic Mortar Test			
	Pressure — Kilograms per sq. cm.	Extreme variation in shots	Increase in pressure with increase of 10% nitroglycerine,	Ratio of extreme variation to increase with 10% more nitroglycerine	Expansion—cc.	Extreme variation in shots	Increase in expansion with increase of 10% nitroglycerine	Ratio of extreme variation to increase with 10% more nitroglycerine.	Recoil—Degrees	Extreme variation in shots	Increase in recoil with increase of 10% nitroglycerine.	Ratio of extreme variation to increase with 10% more nitroglycerine
20....................	54.9	4.9	7.1	.69	128.7	15.3	60.5	.25	14.25	.40	1.18	.34
30....................	62.0	3.2	8.8	.36	189.2	6.4	57.0	.11	15.43	.15	1.96	.08
40....................	70.8	7.6	19.0	.40	246.2	13.4	42.2	.32	17.39	.40	1.42	.28
50....................	89.8	4.0	3.0	1.33	288.4	14.9	26.6	.56	18.81	.40	1.14	.35
60....................	92.8	5.0			315.0	19.6			19.95	.30		

The average "ratio of extreme variation to increase with 10% more nitroglycerine" amounts to:

Druckmesser Test	.69
Trauzl Test	.31
Ballistic Mortar Test	.26

Taking either set of figures, the checks obtained between duplicate tests in the Mortar are therefore better than those obtained in either the Druckmesser or Trauzl tests.

The next point is the question as to whether any of the tests are affected by other qualities than strength. We have found that certain types of explosives, especially those which contain a large amount of ammonium nitrate, shoot proportionately lower in the Trauzl Block than in the Druckmesser or the Ballistic Mortar. Take, for example, the results obtained on a nitrate of ammonia explosive, containing 80% ammonium nitrate, as compared with 60% nitroglycerine dynamite and trinitrotoluol. The figures are given in Table VII.

TABLE VII

EXPLOSIVE	Ballistic Mortar Recoil given by 10 grams of explosive—Degrees	Druckmesser pressure produced by 100 grams explosive in 15 liter chamber—Kg. per sq. om.	Trauzl Block Expansion produced by 10 grams explosive—cc.
Trinitrotoluol	18.80	38.7	242.5
60% Nitroglycerine Dynamite	19.90	45.6	290.1
80% Nitrate of Ammonia Explosive	20.64	52.7	227.2

The Mortar and Druckmesser tests agree in the order of rating of the three explosives, showing trinitrotoluol to be the weakest and the nitrate of ammonia explosive the strongest. In the Trauzl Test, however, the last named explosive shoots much lower than 60% dynamite and lower even than trinitrotoluol. The Trauzl Test rating of the 80% nitrate of ammonia explosive corresponds with that of a 40% nitroglycerine dynamite. This nitrate of ammonia explosive, however, has been used in quarry work in competition with the nitroglycerine grades, and has been found to be stronger than 60% dynamite. The expansion given thereby in the Trauzl Test is accordingly not a true measure of the strength of the explosive. To obtain further information on this point, two ammonium nitrate explosives were made, on the same formula, except that in one the ammonium nitrate used was the standard product regularly used in explosives, while the ammonium nitrate used in the other had been ground and was much finer than the regular product. The two explosives were tested in the Ballistic Mortar, the Druckmesser, and the Trauzl Block, with results as follows:—

	No. 1 Standard Ammonium Nitrate	No. 2 Finely Ground Ammonium Nitrate
Ballistic Mortar—Recoil in degrees................	20.64	20.79
Druckmesser —Pressure Kg. per sq. cm..............	52.7	50.0
Trauzl Block—Expansion in cc....................	227.2	293.4

In the Mortar and Druckmesser Tests, the two explosives shot practically equal, but in the Trauzl Test No. 2, made with finely ground ammonium nitrate, gave an expansion 66.2 cc., or 29% greater than No. 1, made with standard ammonium nitrate. The Trauzl expansion of No. 1 corresponds to that of a 40% nitroglycerine dynamite, while No. 2 gives an expansion greater than of that a 60% nitroglycerine dynamite. The Mortar and Druckmesser tests rate both explosives as stronger than 60% nitroglycerine dynamite. The two explosives did not differ greatly in velocity of detonation. No. 1 had a velocity of 3600 meters per second, while the velocity of No. 2, made with very fine ammonia, was

3960 meters per second. We have found however, as stated earlier in this paper, that the velocity of that portion of a column of dynamite which is close to the detonator is not always the same as the velocity of the remainder of the column, and it was believed that this was true in the case of these two explosives. To obtain evidence on this point, 10 gram samples of each were packed into cartridges $\frac{7}{8}''$ in diameter, primed with a detonator, and shot in contact with a lead plate 4 inches square and 1 inch thick. Each detonation made a regular, concave depression in the lead, similar in form for the two explosives, but very different in diameter and depth. The depression made by explosive No. 2, in which fine ammonia was used, had a capacity (measured with water) more than twice as great as that made by No. 1, showing that in an amount as small as 10 grams, the weight used in the Trauzl test, the two explosives were very different as regards quickness. The difference between the Trauzl tests given by the two was therefore undoubtedly due to this difference in quickness. This is one illustration of a fact which we have found to be generally true, that the Druckmesser and Nallistic Mortar tests show strength alone, but that the Truazl test is affected by quickness as well as strength, and that for that reason it cannot be used for comparing the strengths of explosives which differ in velocity of detonation. This fact makes it impossible to employ the Trauzl Test for general comparisons of different types of explosives, and greatly limits its usefulness.

The third point is the question of the cost of the tests, and the speed with which they can be made. With a crew of two men, twelve or fifteen shots can be made in the Druckmesser in a day, or about seven shots per man. To test one explosive with three different Druckmesser surfaces, making five checking shots with each, a total of fifteen shots, it accordingly requires a full day. One man can make thirty Trauzl tests in a day, weighing out his shots and measuring the expansions. With two molds, two men can cast thirty blocks in a day, just about keeping pace with the tests. Including casting the blocks and making the shots, we therefore make about ten Trauzl tests per man per day. In the Ballistic Mortar, three men can make about one hundred and fifty shots in a day. We find it necessary, however, to make two shots with blasting gelatine before every shot of the explosive which is being tested, to keep the bore of the mortar uniformly clear of solid residue, and to obtain closely checking results, so only about fifty shots of the explosives tested can be made per day, or about sixteen shots per man. All three tests are rather expensive, if properly carried out, but it will appear from these figures that the Mortar Test is the least expensive of the three.

To recapitulate briefly:—

We believe that the best tests for explosives are those which show one quality alone, without being materially affected by variation in other qualities, and we accordingly require quickness or velocity of detonation tests which are unaffected by strength, and strength tests which are independent of quickness.

For quickness or velocity of detonation, we find the Lead Block Compression Test useful as an approximate test, but of limited value, first, because it does not give definite figures, and second, because of the fact that the velocity of detonation of the first few inches of a column of explosive, which is all that the Lead Block Test shows, is not always the same as the velocity of the explosive farther along in the column. The Bichel Test and the Dautriche Test for velocity of detonation are both very satisfactory.

Three tests for strength have been used at the Eastern Laboratory: the Druckmesser Test, the Trauzl Block Test, and the Ballistic Mortar Test. Of these the Druckmesser Test is the only one by which the actual pressure developed by the detonation of an explosive can be determined directly, and for this reason the test is very valuable, in spite of the fact that it is expensive, and that duplicate determinations do not agree as well as in the other two tests.

The variation among duplicate shots is rather less in the Mortar Test than in the Trauzl Test, and the Mortar Test is the more convenient and rapid of the two. For these reasons, the Mortar Test would be preferred if the two tests were otherwise equal. The Trauzl Test has, however, the added disadvantage that with explosives of different types it does not show relative strength, but the results obtained are affected by the quickness of the explosive tested. For this reason especially, the Trauzl Test is used very little at the Eastern Laboratory at present. The Ballistic Mortar Test, which does not have this disadvantage, has been carefully standardized at the Eastern Laboratory, and in its improved form, which is described in a separate paper before this Congress, is used almost exclusively for the rapid determination of the strength of explosives.

(*Abstract*)

THE HYDRONITRIDES

A. L. Kibler
Washington, D. C.

The chemists of the United States have devoted comparatively little attention to the remarkable physical and chemical properties of the hydronitrides. L. M. Dennis of Cornell University made some valuable additions to our knowledge of the character and chemistry of hydronitric acid, but no one has investigated the explosive properties of the salts of this acid with the idea of utilizing them in a practical way. The experiments of Wöhler, Will, Lenze and others in Germany have demonstrated their superiority over mercury fulminate and the possibility of their substitution, in whole or in part, for the latter substance, resulting in greater economy and a more complete utilization of the powder charge. There still remains much work to be done on this line, however, before the hydronitrides can find extensive practical application and it is with the hope of directing the attention of the research chemists of this country to this line of investigation that this paper is presented.

It was my good fortune years two ago to spend a Semester at the Karlsruhe Technische Hochschule in Germany, where I devoted the largest part of my time to a study of the hydronitrides under the able direction of Dr. L. Wöhler, one of the foremost German investigators in this line of chemistry. Dr. Wöhler has published some of the results of this work under the caption "Über Initialzündung" in the Zeitschrift für angewandte Chemie, Vol. *44*, p. 2089, 1911, but some details and results not published will be of interest to chemists engaged in this line of work.

The hydronitrides may be easily prepared by digesting a solution of sodium hydronitride with a solution of a soluble salt of the metal whose hydronitride is desired. The salt falls out in the form of fine crystals which may be filtered with suction, washed with alcohol and ether and dried in a vacuum desiccator. Sodium hydronitride can hardly be termed an explosive body and may be handled without precaution but the salts of all the heavy metals must be handled with the greatest care. The formation of large crystals should be avoided as severe accidents have resulted from the spontaneous explosion of large sized crystals even under water. The small crystals precipitated from concentrated solution may be handled with comparative safety but the operator should always be protected from accidental explosions.

Tests for the sensitiveness of these substances were carried out by the following methods:

1. Sensitiveness to blow was determined by the use of a fall-hammer constructed for the purpose by Wöhler and Matter. The hammer carried a weight of 500 grams and could be dropped from a height of 300 mm. perpendicular distance. The shock was transmitted to 0.05 gm. of the explosive to be tested contained in a small copper cap and compressed with a definite pressure, through a long plunger which fitted snugly in a guide hole. The plungers were of hardened steel and were beveled off at the end to a diameter of about 1.5 mm. It is very important for comparative tests that these ends be carefully ground and of equal size, and they must be examined with a magnifying glass after each experiment to see that no cracks or rough places have developed. The accuracy of these tests depends entirely upon these precautions. With proper care the fall which causes a detonation may be determined within 5 mm. With the most brisant of explosives the plunger is so much injured by the explosion that it must be changed after each test and the cap containing the sample is completely shattered. Of course this extreme brisance would prevent the use of these bodies in guns without admixtures or other device.

2. Sensitiveness to heat was determined by placing a small quantity of the explosive to be tested within a large copper cartridge fixed in a board and plugged loosely with a piece of raw cotton. The cartridge was immersed for a definite length of

time (5 sec.) in a bath of soft bismuth metal held at a constant temperature. Should no explosion occur the sample was thrown out, the cartridge cooled and the experiment repeated after raising the temperature of the bath 5°. Care is taken to adjust the length of the cartridge projecting below the wood that it dip within the bath to the same distance as the thermometer bulb. The point of explosion may be determined with accuracy within 5°. This test is comparative and its success depends upon the accuracy with which the duration of the immersion is timed.

3. Brisance was determined by using varying amounts of the explosive to be tested as a primer on a fixed amount of a standard explosive, such as trinitrotoluene. The smallest quantity completely detonating the main charge was noted. The main charge of 0.5 gm. was first loaded in a copper cartridge of appropriate size and pressed down with a definite pressure—usually 500 gms. A few grains which had been kept out at first were then dropped in and the priming charge added. A small perforated cap was then dropped into the cartridge and pressure again applied. The cartridge so prepared was fitted with a fuse and fixed, by means of an iron contrivance, in an upright position on a square block of lead about 3 mm. in thickness. The nature of the resulting explosion may be very accurately determined by the character of the markings left on the lead plate.

The following results obtained by the above described methods are interesting.

With the fall-hammer the following substances detonated at the heights designated:

Mercury fulminate	75mm.	
Silver fulminate	135 "	
Sodium fulminate	300 "	(120 g. extra wt.)
Nitrogen tetrasulphide	45 "	
Diazobenzene nitrate	50 "	
Lead hydronitride	225 "	
Cupric Hydronitride	110 "	
Cuprous Hydronitride	260 "	
Sodium Hydronitride	not at 300 with 320 gms. extra wt.	

The sensitiveness of the hydronitrides particularly varies between large limits with different sized crystals. The larger the crystal the more sensitive the substance. As already mentioned large crystals may detonate spontaneously. The above figures were obtained by using the smallest crystals, precipitated from concentrated solutions. Under these conditions the hydronitrides are shown to be far less sensitive to shock and blow than the fulminates.

In the priming tests the following interesting results were obtained using 0.5 gm. trinitrotoluene as the main charge. To completely detonate this required:

0.25	gm.	Mercury fulminate
0.20	"	Silver "
0.03	"	Lead Hydronitride
0.02	"	Silver "
0.02	"	Mercury fulminate with 0.01 gm. PbN_6
0.05	"	N_4S_4 with 0.04 gm. PbN_6 superimposed.

Nitrogen tetrasulphide alone has small initial velocity and does not detonate on ignition. If this initial velocity is raised by the addition of even a trace of hydronitride it becomes highly brisant. It appears from the above results that the hydronitrides are from 8 to 10 times more powerful than the fulminates as priming agents. This difference is due to the comparatively small initial velocity of the fulminates which, however, may be so increased by a trace of a hydronitride (0.01 gm. or even less) to act as initial primer that it becomes even more powerful than the hydronitrides themselves.

(*Abstract*)

THE SYNTHESIS OF MERCURY FULMINATE FROM PROPYL ALCOHOL

A. L. Kibler
Washington, D. C.

The following paper is drawn from the experimental part of a Doctor's thesis prepared under the direction of Dr. Chas. E. Munroe of the George Washington University. The work was undertaken with a view to obtaining some new data which might throw additional light on the constitution of the fulminic acid molecule or on the process by which the fulminates are produced. It is well known that the substitution of acetaldehyde for ethyl alcohol in the fulminate process gives a much smoother reaction and a better yield of fulminate and this fact has been cited as proof that aldehyde is the first step in the transformation of alcohol into fulminic acid. Notwithstanding some discouraging and negative results obtained by well known chemists in this field it was proposed to make a close study of the reactions and resulting products obtained by introducing polycarbon compounds into the fulminate process in place of the usual ethyl alcohol. Since aldehyde seems to be a step in the process particular attention was to be paid to the behavior of the higher aldehydes. If the alcohols and aldehydes of higher carbon content should produce bodies which could be considered as substituted fulminates or as related to the fulminates, then the analysis and composition of these bodies would give valuable information on the constitution of the fulminates themselves, while, on the other hand, if these substances should yield true fulminates some light might be thrown on the so-called "fulminate process." Accordingly the experiments described below were undertaken.

I had at my disposal, in addition to the ordinary methyl and ethyl alcohols, amyl alcohol, isobutyl alcohol and normal propyl alcohol, in addition to which acetone was also used. Aldehydes were prepared from ethyl and propyl alcohols.

In no case in which one of the above mentioned polycarbon compounds was substituted in the fulminate process and the reaction was allowed to continue according to the usual method were compounds at all analogous to the fulminates obtained. Some compound was indeed usually obtained but examination under the microscope almost invariably showed the presence of considerable quantities of metallic mercury and, where this was not revealed by the microscope, there was no certainty that metallic mercury was not present in small quantities, being enclosed in the amorphous granules. Furthermore the compound is very unstable and the amount of metallic mercury present in it increases steadily on standing. On this account all attempts at identification have thus far proved fruitless. L. Wöhler, whose well known molecular weight determination on sodium fulminate has furnished the final proof of the monocarbon constitution of fulminic acid, considered these bodies oxalates but I was not able to identify them as such.

In the course of experiments with acetone, amyl alcohol, isobutyl alcohol, propyl alcohol and propaldehyde the following significant observations were made:

1. The end product was in every case identical so far as their properties could be tested. All were composed of round or oval amorphous granules, yellowish in color and mixed with more or less metallic mercury. Dried and burned on filter paper they burned slowly with faint scintillating sparks.

2. The nature of the precipitate changed on the addition of water at the end of the reaction, becoming gummy, yellowish gray in color, and disengaging gas which sometimes was evolved so rapidly as to bring the heavy precipitate to the surface. When first precipitated from the liquid in violent reaction it was apparently of a heavy, granular nature and white in color. On standing, or even when the reaction was allowed to proceed to its end, the nature of this precipitate changed, accompanied by evolution of gas from the crystals themselves.

Encouraged by these results and others pointing to the same conclusion I made the following experiments using propyl alcohol which seemed best suited for my purpose. In order that the various phases of the reaction might be observed more closely the mercuric nitrate solution was poured into the alcohol contained in a 500 c.c. graduate. When the maximum of precipitation had occurred the contents of the graduate while still in violent reaction were poured quickly into a porous alundum crucible and immediately sucked through with strong suction. The graduate, which contained much of the precipitated salt, was quickly filled with water and the precipitate washed into the crucible and thoroughly washed with clean, cold water. The crystals collected proved to be a very pure mercury fulminate. They showed the well known characteristic form under the microscope. They were pure white and contained no metallic mercury. They puffed off sharply on being heated and detonated violently under the hammer. When dissolved in concentrated hydrochloric acid hydroxylamine was produced quantitatively. An analysis for mercury by the electrolytic method gave 70.03% of mercury instead of 70.42% calculated. This new synthesis of mercury fulminate is interesting as being the first time it has been produced from a substance containing more than two carbon atoms.

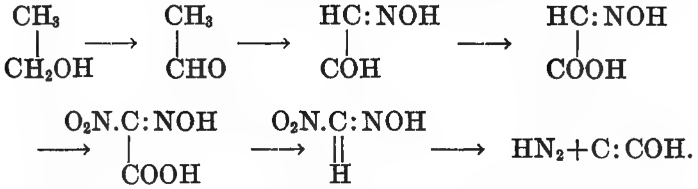
In regard to the purity of the propyl alcohol used, Hoffman and Kropff of Philadelphia, from whom the alcohol was obtained, say "We believe that it is the finest product on the market, and free from ethyl alcohol. Our fractionations are very carefully conducted in this case and columns of about 30 feet in height are employed."

On making the iodoform test for the presence of ethyl alcohol as described by Merck I noted a slight odor of iodoform in a clear solution, whereas the same test made on ethyl alcohol gave immediately a heavy precipitate of iodoform. The specific gravity of the propyl alcohol was 0.801, boiling point 96–96.5°C. (Merck gives 0.8066 and 96–98°C.)

By moderating the reaction with ice water, decanting off and inducing a second and third precipitation I obtained as much as 0.25 gm. of pure mercury fulminate from 1 gm. of mercury and 14 c.c. of propyl alcohol. This calculated to ethyl alcohol is equivalent to 0.16 gm. of alcohol. Assuming that the ethyl alcohol is transformed quantitatively into fulminate the propyl alcohol must contain 1.4% of ethyl alcohol. But the ethyl alcohol could not be transformed quantitatively into fulminic acid. Calculating that only $\frac{1}{17}$ of the alcohol is so transformed, according to Wöhler, the propyl alcohol must have contained 24.2% of ethyl alcohol. But from the tests made on the alcohol as well as the statement of the manufacturer it must contain but slight traces of ethyl alcohol if any. Clearly the fulminate is formed from the propyl alcohol itself.

It is interesting to note that with the use of propyl alcohol I have isolated and examined an intermediate product in the fulminate process though I have not as yet identified it. Soon after the two solutions are mixed and before the violent reaction begins there is sometimes deposited a quantity of light, flaky crystals which again go into solution when the reaction begins. Some of these crystals were drawn out and drained of their acid on a watch glass and examined under the microscope. They consisted of perfectly formed, large, lustrous, white plates, the longer dimension of which was about five times the shorter. They were highly unstable decomposing spontaneously, and when treated with water, leaving only traces of a grayish powder, probably metallic mercury. The crystals were not explosive when heated but vaporized rapidly leaving hardly a trace of solid matter. There is no doubt that these crystals are crystals of one of the much sought intermediate products of the fulminate process which, in the case of the propyl alcohol is either less unstable than the corresponding compound from ethyl alcohol or is crystalline whereas the corresponding ethyl alcohol derivative is liquid.

Wieland's theory as to the different stages of the reaction by which fulminic acid is obtained from ethyl alcohol, (B. *40*, 418–422, 1907) may well explain why the mercury fulminate obtained from propyl alcohol is decomposed during the last stages of the reaction, and his theory receives confirmation to the extent that it explains this decomposition. Wieland's theory is briefly explained in the following scheme of formulae:



$$\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{CH_2OH}\end{array}\longrightarrow\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{CHO}\end{array}\longrightarrow\begin{array}{c}\mathrm{HC{:}NOH}\\|\\\mathrm{COH}\end{array}\longrightarrow\begin{array}{c}\mathrm{HC{:}NOH}\\|\\\mathrm{COOH}\end{array}$$

$$\longrightarrow\begin{array}{c}\mathrm{O_2N.C{:}NOH}\\|\\\mathrm{COOH}\end{array}\longrightarrow\begin{array}{c}\mathrm{O_2N.C{:}NOH}\\\|\\\mathrm{H}\end{array}\longrightarrow\mathrm{HN_2+C{:}COH.}$$

According to this theory when propyl alcohol is substituted for ethyl alcohol methyl nitrite would be formed in the last stage of the reaction instead of nitrous acid, and methyl nitrite, being a much more unstable body than nitrous acid itself, decomposes liberating nascent NO_2 which attacks the fulminate. Further confirmatory evidence of this reaction is found in the strong fruity odor given off during the reaction which might well be the odor of methyl nitrite.

I have not yet been able to obtain any fulminate from the other polycarbon alcohols used. Some preliminary experiments were unsuccessful. From the identity of the final products, however, it seems probable that further work along this line may be rewarded by the production of fulminates from various polycarbon alcohols and indeed from acetone itself.

DEVELOPMENT IN EXPLOSIVES IN THE UNITED STATES DURING THE LAST THREE YEARS

PROF. CHARLES E. MUNROE
Washington, D. C.

Since my report of progress to the Congress at London another census of manufactures, including explosives, has been taken by the United States. The data obtained for the Explosives Industry is presented in comparison with that obtained for the next two previous censuses in Table I, in which not only the principal products obtained, but also the chief materials used in the manufacture are given.

The production of explosives in the industry proper was 469,481,252 pounds in 1909, 360,980,734 pounds in 1904, and 215,980,720 pounds in 1899, an increase for the decade of 117.4 per cent. If the explosives made by establishments operated by the Federal Government and by establishments engaged primarily in the manufacture of other products be added, the total production in 1909 was 471,446,006 pounds. The output of dynamite formed about three-eighths of the total output of explosives, and its value approximately one-half of the total value of explosives reported. The most important product in respect to quantity of output, namely, 233,477,175 pounds, was blasting powder. Permissible explosives were reported separately for the first time in 1909. They are specially designed for use in dusty and gaseous coal mines. The production of smokeless powders, chiefly cellulose nitrate powders, is included in the returns for "other explosives," but there has been a steady increase in their manufacture.

In my report for 1909 attention was called to the progressive deterioration of straight cellulose nitrate powders of low nitration and of the provision made by the United States officials for the reworking of such powders. An unexpected use was made of this in the commercial competition between the manufacturers

TABLE I

Quantities and Values of Explosives Produced in the United States

MATERIALS	1909	1904	1899
Total cost	$22,811,548	$17,203,667	$10,334,974
Nitrate of Soda:			
Tons	188,889	133,034	88,524
Cost	$7,892,336	$5,608,557	$2,902,866
Acids:			
Mixed—			
Pounds	51,764,694	105,552,404	66,906,146
Cost	$1,512,626	$3,093,429	$1,505,754
Nitric—			
Pounds	7,591,756	2,699,500	467,587
Cost	$541,314	$122,047	$17,171
Sulphuric—			
Tons	22,501	18,298	7,864
Cost	$406,204	$247,301	$130,699
Sulphur or brimstone:			
Tons	17,389	19,574	12,742
Cost	$367,866	$507,469	$317,383
All other materials, cost	$12,091,202	$7,624,864	$5,461,101
PRODUCTS.			
Total value	[1]$40,139,661	[2]$29,602,884	$17,125,413
Dynamite:			
Pounds	177,155,851	120,920,829	85,846,456
Value	$18,699,746	$12,900,193	$8,247,223
Nitroglycerine, sold as such:			
Pounds	28,913,253	7,935,936	3,618,692
Value	$3,162,434	$1,620,117	$783.299
Blasting powder:			
Kegs (25 pounds)	9,339,087	8,217,448	3,907,012
Value	$9,608,265	$7,377,977	$3,857,974
Permissible explosives:			
Pounds	9,607,448	....	....
Value	$863,209	....	....
Gunpowder:			
Pounds	12,862,700	10,383,944	25,638,804
Value	$1,736,427	$1,541,483	$1,452,377
Other explosives:[3]			
Pounds	7,464,825	6,303,825	3,201,468
Value	$3,913,787	$4,256,193	$2,610,103
All other products, value	$2,155,793	$1,906,921	$174,442

[1] In addition, 1,481,042 pounds, to the value of $802,948, were made by Federal establishments, and 219,356 pounds, to the value of $135,979, by establishments engaged primarily in the manufacture of products other than those covered by the industry designation.

[2] In addition, 1,104,532 pounds, to the value of $690,032, were made by Federal establishments and by establishments engaged primarily in the manufacture of products other than those covered by the industry designation.

[3] Includes smokeless powder and guncotton or pyroxyline, to avoid disclosing operations of individual establishments.

NOTE.—The following products were made and consumed in the establishments where produced:

		1909	1904
Saltpeter	pounds	12,050,225	3,559,376
Nitroglycerine	pounds	70,289,667	44,077,828
Sulphuric acid	tons	42,555	30,994
Nitric acid	tons	31,484	18,988
Charcoal	bushels	737,884	1,156,918
Cellulose nitrates	pounds	5,000,226	....
Nitrate of ammonia	pounds	10,904,319	6,299,317

of powders of this type of base and those manufacturing the nitroglycerine-nitrocellulose powders of the Cordite type which was voiced in many articles appearing in London *Engineering*, hence it is proper to say here that even at the time when my paper appeared in print the United States Government had adopted diphenylamine as an additional component of its service powder, that this material has been found to act as an efficient stabilizer, and it is held "that powders which in themselves would have a safe life of six or seven years can be confidently counted upon, if containing diphenylamine, for a life of twenty years, and perhaps much more than this." The reworking of old type powder has gone on, the material being converted to use in the new type. This reworking is most profound in character, the grains being reduced to dust, and this finely comminuted cellulose nitrate thus produced being put through the same purification treatment as that to which freshly produced cellulose nitrate is subjected before being compounded into the finished powder. A comparison of the methods show that the process differs intrinsically from the superficial "radoubage" practised by the French.

Naturally this comment on the stability of cellulose nitrate powders of low nitration, coupled with the fact that several accidents had occurred on naval vessels to which they were supplied aroused apprehension among the officers and men aboard, and to determine the facts in the case the editorial in *Engineering* for October 6, 1911, was referred for consideration and comment to the United States Joint Army and Navy Powder Board. The report of this Board is published in the United States Naval Institute Proceedings, Vol. 38, pages 133 to 179, and it justifies the action of the United States Ordnance Bureau in selecting the powder now adopted for its Army and Navy. The improvement in *morale* following this publication demonstrates that publicity is as necessary and beneficent in military as in industrial and commercial operations and that in all the real activities of man, secrecy is frequently most costly and eventually entails great loss in efficiency.

The Bureau of the American Railway Association for the Safe Transportation of Explosives and Other Dangerous Arti-

TABLE II

Work of Bureau for Safe Transportation of Explosives, A. R. A.

	1911	1910	1909	1908
Total number of railway lines members of Bureau, December 31st...	228	174	172	158
Total mileage of Bureau lines, December 31st..................	236,211	228,986	209,984	202,186
Total number of steamship lines members of Bureau, December 31st...	11	11	....	....
Total number of express companies members of Bureau, December 31st	3	2	....	....
Total number of associate members of Bureau, December 31st......	30	32	83	....
Total number of inspections of stations.........................	8,572	8,031	6,593	5,603
Total number of inspections of factories........................	274	315	278	270
Total number of inspections of magazines........................	1,561	1,528	1,292	1,540
Total number of boxes of high explosives condemned as unsafe for transportation..	6,591	10,902	10,029	4,852
Total number of kegs of black powder condemned as unsafe for transportation..	1,205	1,291	1,468	531
Total number of boxes of high explosives condemned at factory.....	....	4,913	....	....
Total number of cars in transit containing explosives inspected......	1,412	647	475	448
Total number of cars in transit showing serious violations of regulations...	210	235	168	197
Total number of express inspections..............................	1,027	....	....	....
Total number of inspections of steamship companies' piers..........	72	69	69	....
Total number of inspections made by Bureau....................	12,919	18,615	16,087	8,959
Total number of lectures to railway officials and employees, and meetings addressed on the subject of safe transportation of explosives and other dangerous articles......................	637	228	215	171

cles, whose organization I announced at London, is now firmly established and the results accomplished are shown in Tables II and III from the Fifth Report of the Chief Inspector.

During the same period reports have been rendered to the Chief Inspector by the Chemical Laboratory of the Bureau on 955 samples.

With the completion of the organization and the remedying of the most obvious evils, much attention has been given to researches, the results of which have appeared in the Annual Reports of the Inspector. Col. Dunn made a most elaborate investigation into the methods of loading cars, which resulted in the "Methods for Loading and Staying Carload and Less than Carload Shipments of Explosives," published with diagrams January 2, 1911, as B. E. Pamphlet No. 6, while Chief Chemist Beistle has secured positive results in the promotion of safety in his studies of exudation of nitroglycerine alone and when mixed with nitrotoluol in dynamites; spontaneous ignition in railway torpedoes and time-signal railway fusees; stability of nitro-starch explosives; safety of chlorate explosives, and a variety of other topics, the conclusions regarding which

TABLE III

Accidents in Transportation of Explosives 1907 to 1911, Inclusive

	1911		1910		1909		1908		
	In Transit	On Railway Property Awaiting Removal by Consignee	In Transit	On Railway Property Awaiting Removal by Consignee	In Transit	On Railway Property Awaiting Removal by Consignee	In Transit	On Railway Property Awaiting Removal by Consignee	In Transit and on Railway Property Awaiting Removal by Consignee
Number of accidents resulting in explosions or fires in transportation *of explosives* by rail	8	2	5	11	3	9	9	13	79
Known property loss on account of explosions or accidents in transporting explosives by rail	$26,611	$8,150	$31,909	$11,727	$1,537	$1,136	$24,919	$89,710	$496,820
Number of persons injured by explosions in transportations	2	3	....	1	2	5	8	45	80
Number of persons killed by explosions in transportation	1	......	2	......	4	2	16	10	52
Total known property loss	$34,761		$43,636		$2,673		$114,629		$496,820

are set forth in the successive annual reports of the Chief Inspector. Appended to the report for February, 1912, is a detailed, illustrated report on the disastrous explosion which occurred at Communipaw, N. J., on February 1, 1911. This is an earnest of what may be expected in the future though a detailed official report on the explosion at the New York Central Station has not yet appeared.

The regulations formulated by this Bureau have proved so excellent and workable that they have been adopted and promulgated by the United States Interstate Commerce Commission, and they now govern all railroads in the United States engaged in interstate commerce. It is believed that the legislation relative to the operation of the Panama Canal may give this body control over interstate transportation by water also. As chairman of the Advisory Committee of the American Railway Association, with Dr. H. S. Drinker, President of Lehigh University, and Dr. Charles F. McKenna as associates, which, in 1905, reviewed and passed upon this subject, it is gratifying to note the progress that this Bureau has made and the success it has achieved. The conception and initial direction was due to our lamented associate, Dr. Charles B. Dudley, who, from the founding of the Bureau in 1907 until his death, served as its President. The practical operation has throughout been in the competent hands of Col. B. W. Dunn, and with Dr. Dudley, he has made the Bureau a most valuable aid to the State and an efficient protector of life and property.

The Pittsburgh Testing Station of the United States Bureau of Mines, which was, as stated in my last report, opened in September, 1908, and which in January, 1909, became ready to make official tests of explosives for use in coal mines containing gas, gas and dust, or dust in dangerous quantities, had, on January 1, 1912, established a list of 77 Permissible Explosives. Several score more of the different explosives submitted in these three years of operation passed the required tests and were admitted to the list, but have subsequently been withdrawn because of their manufacture not having been continued, or for other reasons. All of these explosives must not only pass the three sets of gallery tests in which the atmosphere is charged with definite quantities of natural gas, or bituminous coal dust, or both, as prescribed, but they must also satsify all the requirements of exudation, stability and other chemical tests, and also give satisfactory results in the ballistic pendulum, pressure gauge, calorimeter, Trauzl, small lead block, impact, rate of detonation, flame and frictional pendulum tests. The equipment of the Station is described and illustrated in detail in Bulletin 15 of the Bureau of Mines. The frictional pendulum is an exception to this, since it has been devised and constructed since that Bulletin was written. It embodies in mechanism the principle of Duprés' famous broomstick test, in which the explosive is exposed to a glancing blow. It comprises a steel anvil with a smooth face 3¼ inches wide by 12 inches long, in the middle of which are three grooves for holding the explosive, and a swinging steel shoe having a radius of swing of 6 feet 6¾ inches and a radius of curvature to its face of 10½ inches. The shoe can be, and in practice is, faced with hardwood fibre or other material. The shoe may be dropped from heights of one-half to 2 meters and weights of 1 to 20 kilos are used in the tests. The apparatus has now been in use about one year and has given most satisfactory results. This Bulletin reports also the data obtained with the first 17 permissibles tested, as well as that obtained in the tests of 4 foreign explosives which had passed the tests abroad. The object of these, and of other tests of foreign explosives now being made, is to discover, if possible, means by which to correlate the results obtained by foreign testing stations with those obtained at Pittsburgh in spite of the differences existing in the forms and dimensions of the different galleries; the nature and proportions of the gases used; the unlike methods of stemming and firing; and in other particulars.

Many researches have been carried out or are being carried out at this station. The results of investigations into the explosibility of coal dust; of mine gases and dusts; of the characteristics of fuse and squibs with the influence of temperature and pressure on the rate of burning of fuse; the effect of stemming on the efficiency of explosives; and the behavior of nitroglycerine when heated have already been published. This last daring investigation was carried out by Dr. W. O. Snelling and C.

G. Storm, who effected the distillation of nitroglycerine (accompanied, however, by decomposition); determined its ebullition point as 145°; its explosion point (by thermocouples immersed in it) as 218° ±5°; and proved its progressive exothermal decomposition, starting between 50°–60° and becoming rapid at 135°.

An investigation of marked practical value by Clarence Hall and Spencer P. Howell is published as Technical Paper 18 under the title "Magazines and Thaw Houses for Explosives," and gives precise details for the construction of such buildings from cement-mortar blocks made of 1 part cement to 6 parts coarse sand. These blocks were found to offer greater resistance to bullets than the sand or mineral wool heretofore used in this country for filling in the walls of such structures. They presented less resistance to penetration than concrete, but have the advantage over the latter that, when exposed to an explosion, they are shattered to dust. A magazine having a capacity of 20,000 to 30,000 pounds of explosives was built of this material at a cost of $400.

As the explosives which are placed on the Permissible List must, when offered for sale, be identical with the samples tested, all explosives submitted for test are carefully analyzed as a part of the means for subsequent identification. This has necessitated the devising of methods for the analysis of the many new compositions of matter presented. In order that the manufacturers and consumers may be able to check and use the methods of identification, these methods are described with fulness in a bulletin now in process of publication and which will be followed by others as additional methods are proven to be of value. The study of the characteristic behaviors of the components of these mixtures, which is essential to the development of analytical methods of separation and identification, has led to some interesting discoveries which are soon to be made public.

Much attention has been given to the development of poisonous products in explosions, and more especially carbon monoxide, the gases being collected for study not only from the pressure gauge, but also from the face of the breast in the mines. A tentative maximum limit for CO, of 158 liters from 680 grams, which permissible explosives must not exceed, has already been fixed, but farther studies in the mine are being made and a mechanical sampling device has been invented for taking the gas samples without exposing the person unduly. Chronic poisoning by continued exposure to small amounts of CO is also being made a subject of study as a guide in fixing the permissible limits of this gas in explosion products.

The Bureau has also conducted a campaign of education among operators and miners by means of publications such as "A Primer on Explosives for Coal Miners," and "Miners' Circulars"; by lectures; and by demonstrations with the gallery and other appliances at Pittsburgh, and, recently, with portable galleries which are carried into the mining districts. As a result of this the quantity of short flame explosives, including permissibles, manufactured in 1909 exceeded by 1,265,897 pounds the entire quantity of such explosives manufactured in this country from 1902, when the manufacture first began, up to 1909. No statistics are available for 1910 and 1911, but it is estimated that the manufacture is now twice as great as in 1909.

A large measure of the general increase in the production shown in Table I has been due to the rapid growth in their use in this country in agriculture, where they are used not only in breaking boulders, blowing up stumps, excavating holes in which to plant trees, and in cultivating the under-soil, but also in driving irrigation and drainage ditches following the method I devised in 1898 for throwing up military intrenchments with dynamite, while condemned gunpowder is being used directly as a nitrogenous fertilizer with which to raise crops. Among the large projects using explosives may be named the Panama Canal, which, in the last three years, consumed 32,500,000 pounds of dynamite, and the Croton Aqueduct some 20,000,000 pounds.

A commercial feature of the industry has been the increased cost of glycerine during the last three years, it having in 1910 reached the extraordinary price of 24¼ cents per pound. The scarcity of glycerine and the scarcity of bone for use in the phosphate industry throw curious side lights on the increased cost of meat. This high cost of glycerine has stimulated researches looking to the production of synthetic glycerine and glycols. The improvements in methods now announced for the cheapening of the cost of the production of propyl alcohol is an important step in this direction. The recovery by Dr. Snelling of large quantities of ethane, propane and butane from natural gas, and their subsequent separation, is another step. A development which is accomplished and which promotes the industry is that of the separation of toluene[1] and the manufacture of nitrotoluenes from water gas tar, since this increases our visible supply of raw material for the nitrosubstitution explosives which are entering so rapidly into use in recent times.

[1] By-Products in Gas Manufacture. Charles E. Munroe. Centenary Lectures, American Gas Institute, 28–66, 1912. Also J. Frk. Inst. June, 1912.

COMMISSION INTERNATIONALE POUR L'ÉTUDE DE L'UNIFICATION DES MÉTHODES D'ÉPREUVES SUR LA STABILITÉ DES EXPLOSIFS

Rapport Final approuvé le 25 juillet 1912, pour être présenté au VIII^{me} Congrès international, à Washington-New-York (septembre 1912)

I.—Aperçu Général des travaux de la Commission

Avant de formuler nos conclusions dans ce rapport qui fait suite à ceux qui ont été déposés à Londres en 1909 et qui sont insérés dans les Publications du VII^{me} Congrès, volume traitant des travaux de la section III*b* (Explosifs), pages 130 à 190, nous rappellerons succinctement quels ont été, depuis le début, les travaux de la Commission, comment celle-ci a fonctionné et par quelles voies elle est arrivée aux conclusions que nous proposons à la ratification du VIII^{me} Congrès de Chimie appliquée, à Washington-New-York, en 1912.

C'est à Rome, en 1906, au VI^{me} Congrès de Chimie appliquée, que la Commission a été instituée. La section III*b* (Explosifs) du dit Congrès ayant reconnu l'opportunité d'unifier les méthodes d'épreuves sur la stabilité des explosifs, a nommé une Commission internationale[1] chargée d'étudier cette question et de pré

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[1] Ont été désignés pour faire partie de cette Commission:

Pour l'*Allemagne:* MM. Professeur W. Will, à Berlin; Professeur H.-F. Lenze, à Charlottenburg; Professeur F. Heise, à Bochum; Directeur général C.-E. Bichel, à Hambourg;

Pour l'*Espagne:* M. M. Jacqué, à Bilbao;

Pour la *France:* M. L. Barthelemy, à Paris;

Pour la *Grande-Bretagne:* MM. C.-O. Lundholm, à Stevenson, et Professeur W.-F. Reid, à Addlestone;

Pour l'*Italie:* MM. Colonel G. Vitali, à Rome, et Professeur G. Spica, à Venise;

Pour les *Pays-Bas:* M. le Capitaine Gey van Pittius, à Amsterdam;

Pour la *Russie:* M. Professeur Sapojnikoff, à Saint-Petersbourg;

au Congrès suivant un rapport destiné à servir de base à cette unification.

Dans sa séance plénière du 3 mai 1906, le Congrès a ratifié la décision de la section III*b*, dans les termes suivants:

"Le VIe Congrès international de chimie appliquée, tenu à Rome, en 1906, reconnait la nécessité de voir unifier les méthodes d'épreuves sur la stabilité mécanique et chimique des explosifs, et ratifie la nomination d'une Commission spéciale pour étudier cette question et présenter un rapport au prochain Congrès."

Pour donner suite au vœu du Congrès, il a été adopté séance tenante, à Rome même, le programme suivant:

En premier lieu, s'enquérir des méthodes existantes dans les divers pays et les faire connaître aux membres de la Commission;

Recueillir ensuite les propositions de ceux-ci sur les méthodes qu'il conviendrait d'adopter, soit que quelque méthode existante soit préconisée, soit que de nouveaux procédés soient proposés;

Enfin, chercher une entente sur un système unique.

Pour assurer la réalisation de la première partie du programme le bureau (à cette époque composé de MM. Watteyne et Stassart) a adressé une circulaire à MM. les membres de la Commission en les priant de faire connaître quelles sont les épreuves en usage dans leurs pays respectifs.

Les réponses à cette circulaire, jointes à d'autres renseignements puisés à d'autres sources, ont fait l'objet d'un *premier rapport* daté du 25 mars 1908 qui a été distribué à MM. les membres de la Commission et à toutes les personnes susceptibles d'intervenir utilement dans l'étude dont il s'agit.

Par de nouvelles circulaires, il a alors été demandé à MM. les membres de la Commission de faire connaître leurs propositions justifiées sur les méthodes qu'à leur avis, il conviendrait d'adopter uniformément dans les divers pays.

Ces notes, qui font l'objet d'un *deuxième rapport,* devaient

Pour la *Belgique:* MM. Inspecteur général des mines V. Watteyne, à Bruxelles, et Ingénieur en chef Directeur des mines S. Stassart, à Mons.

MM. Watteyne et Stassart ont été nommés respectivement Président et Secrétaire de la Commission.

M. Stassart étant décédé le 21 janvier 1911, la Commission à désigné, pour le remplacer, M. l'Ingénieur des mines Ad. Breyre, àBruxelles.

servir de base à des discussions finales et à une entente définitive, si toutefois celle-ci était réalisable, au Congrès de Londres.

Mais des circonstances se sont présentées qui ont retardé cette entente finale:

Dans l'intervalle des deux Congrès, le Gouvernement allemand avait mis à l'étude cette même question des épreuves à faire subir aux explosifs pour l'admission de ceux-ci au transport, et, précisément, parmi les personnes chargées de cette étude se trouvaient deux de nos collègues, MM. les professeurs Will et Lenze.

Ces études se sont prolongées presque jusqu'à l'époque du Congrès de Londres. Elles ont abouti à tout un programme d'épreuves à faire subir aux explosifs de diverses catégories.

Ce programme ou plutôt ce règlement, fruit de recherches approfondies et soigneusement élaboré, était à prendre en considération par notre Commission et il a paru à celle-ci qu'il y avait lieu d'attendre que ce règlement eût été appliqué en Allemagne pendant un certain nombre de mois, en vue d'en reconnaître les avantages et les inconvénients. Après une telle expérience, la Commission internationale, disposant ainsi de nouveaux et importants éléments d'appréciation, pourrait se prononcer en meilleure connaissance de cause.

Dans ces conditions, la Commission ne pouvait que proposer au Congrès la prorogation de sa mission jusqu'au Congrès suivant.

C'est ce qui a été décidé, en séance de la Section des explosifs d'abord, et, ensuite, en séance plénière du Congrès, le 2 juin 1909.

Nous ne croyons pas avoir à reproduire les premiers rapports; ceux-ci, condensés, mis à jour et terminés par un projet de conclusions, élaboré par le Bureau, ont reçu une publication suffisante, par le fait de leur insertion dans les publications du Congrès. Ajoutons que les travaux de la Commission jusqu'en 1909 ont été publiés dans les *Annales des Mines de Belgique* (t. XV (1909), 4^{me} livr.,), dans un article de MM. Watteyne et Stassart, intitulé: *Les mines et les explosifs au VII^{me} Congrès international de Chimie appliquée, à Londres, en 1909* (voir pages 90 à 170 du tiré à part.)

Cet article, qui peut être considéré comme un *troisième rapport* de la Commission, reproduit également (pp. 170 à 182) les notes de MM. Kast, Will et Lenze sur les travaux de la Commission allemande, notes qui avaient été produites au Congrès de Londres.

En annexe dudit article de MM. Watteyne et Stassart on trouve aussi, pages 221 à 232 du tiré à part des *Annales des Mines de Belgique*, la traduction française de la partie principale de la nouvelle réglementation allemande.

Conformément à ce qui avait été décidé, on a laissé s'écouler un temps assez long pour que les avantages et les inconvénients du règlement allemand aient pu se manifester; puis le Bureau (MM. Watteyne et Breyre, ce dernier ayant été désigné comme secrétaire en remplacement de M. Stassart) a écrit, en 1911, aux membres allemands de la Commission pour les prier de faire connaître les observations auxquelles avait donné lieu, en Allemagne, l'application du règlement nouveau.

MM. Bichel, Heise, Will, Mente et Lenze (ces trois derniers collectivement), ont répondu respectivement le 29 septembre, le 28 octobre et le 7 novembre 1911.

Par lettre-circulaire du 12 mars 1912 (annexe I), le Bureau fit connaître à tous les membres de la Commission, les observations des collègues allemands et, en même temps, soumettait à l'examen de la Commission un nouvel *avant-projet de conclusions.*

Cet avant-projet, qui forme, avec les notes de MM. Bichel, Heise, Will, Mente et Lenze, l'annexe I au présent rapport, établissait d'abord une classification simplifiée, basée sur les propriétés générales des explosifs au point de vue de la résistance aux causes de danger pendant l'emmagasinage et le transport, puis il suggérait un nombre limité d'épreuves s'appliquant aux diverses catégories et classant dans l'une ou l'autre de celles-ci l'explosif considéré. Une première épreuve s'appliquant à tous les explosifs permettait d'éliminer préalablement tous les produits défectueux.

Le projet de classification indiquait, en grandes lignes, les types d'explosifs qui entraient dans les trois catégories proposées.

L'annexe I donnant ce projet *in-extenso*, nous n'y insisterons pas davantage ici.

A la fin de la lettre du 12 mars, le Bureau demandait aux membres de la Commission de formuler à bref délai leurs observations sur le projet et, en même temps, faisait part du désir émis par plusieurs membres de se réunir en un point central en Europe en vue de permettre à la Commission de se concerter et d'arriver à un accord définitif pour le rapport à présenter au Congrès de Washington-New-York.

Les réponses ayant été formulées par la plupart des membres (MM. Will, Mente et Lenze (collectivement), M. Heise, M. Barthélemy, M. Jacqué, MM. Vitali et Spica et M. Lundholm), et le lieu de la réunion ayant été fixé à Paris, le Bureau a, par sa lettre du 18 mai 1912 (annexe II) porté ces réponses à la connaissance de tous les collègues, en les convoquant pour le 24 juin, à Paris, dans le local que M. Barthélemy mettait à notre disposition.

Dans l'intervalle de la lettre du 18 mai et de la réunion du 24 juin, sont encore parvenues au Bureau diverses notes:

1° Une lettre que M. Gey van Pittius, empêché, par un séjour prolongé aux Indes néerlandaises, de prendre part à la réunion de Paris, écrivait de Malabar en date du 27 avril 1912 (annexe III);

2° Une nouvelle lettre de M. Lundholm, en date du 10 juin (annexe IV);

3° Une nouvelle note, du 22 juin, de M. Jacqué (annexe V).

Le 24 juin 1912, nous nous sommes réunis à Paris, où nous avons été reçus par le collègue Barthélemy.

Ont assisté à cette réunion: MM. Watteyne, président; Barthélemy, Jacqué, Vitali et Will, membres, et A. Breyre, Secrétaire. M. Mente, collaborateur de M. Will, M. le Bergassessor Beyling, Directeur de la Station d'essais de Westphalie, délégué par M. Heise, et M. Schmerber, Ingénieur à Paris, prêtant son bienveillant concours comme interprête, assistaient aussi à la séance.

S'étaient fait excuser MM. Bichel, Gey van Pittius, Heise, Lundholm et Spica.

Après une laborieuse discussion, dont les traits principaux sont relatés dans le procès-verbal de la séance (annexe VI), on s'est mis d'accord sur les points essentiels de nos conclusions que nous allons donner ci-après.

Les travaux proprement dits de la Commission se divisent donc en fait, en deux périodes, celle de 1906 à 1909 et celle de 1910 à 1912; les travaux de la première période sont consignés dans les trois premiers rapports déjà publiés, aux endroits indiqués plus haut; ceux de la seconde période, dans les annexes du présent rapport.

Nous renvoyons à ces documents pour la justification des conclusions qui vont suivre.

II.—CONCLUSIONS

Il résulte des idées échangées et des discussions produites au sein de la Commission que le problème de l'unification des méthodes d'épreuves sur la stabilité des explosifs présenterait des difficultés insurmontables s'il fallait lui donner dès à présent une solution complète, consistant dans l'adoption d'une réglementation uniforme et exclusive s'appliquant à tous les pays.

La multiplicité des explosifs, les conditions et nécessités différentes pour chaque pays et le fait que la plupart des méthodes d'épreuves actuellement connues ne s'appliquent pas également à tous les explosifs, sont parmi les causes de ces difficultés.

Mais nous croyons qu'un pas important sera fait dans l'acheminement vers la solution complète et qu'une amélioration notable de la situation actuelle serait accomplie si, parmi les multiples essais actuellement en usage et différant d'une région à l'autre, on pouvait choisir un petit nombre d'épreuves bien définies, de réalisation aisément uniforme, et qui, par elles-mêmes, classent les explosifs en quelques grandes catégories, de propriété générales communes.

C'est ce choix que la Commission s'est efforcée de faire, laissant à chaque Gouvernement la faculté d'approprier à sa réglementation, dans telles conditions qu'il lui plaira, les principes indiqués.

Leur adoption, ne fût-ce que comme épreuve "de consignation," pour les pays qui désireraient maintenir d'ailleurs leurs procédés et leurs usages, constituerait un progrès sérieux en introduisant, dans les exigences administratives, quelques points de repère qui, en se multipliant dans la suite, feront approcher de plus en plus de l'uniformité désirée.

Tout d'abord la Commission a décidé de restreindre son action aux explosifs *industriels,* à l'exclusion des explosifs de tir et de guerre.

Il en résulte que, dans les épreuves qu'elle propose, elle n'a pas à considérer les explosifs *à base* de nitrocelluloses.

Elle ne vise pas non plus les détonateurs, qui, dans tous les pays, forment une classe bien distincte.

Avant tout, la Commission croit devoir présenter une observation générale sur la question de *l'emballage.*

Elle attire sur ce point important l'attention des Gouvernements: La sécurité du transport ne peut, en effet, être envisagée en faisant abstraction du mode d'emballage, dont l'ordonnation appropriée permet d'équilibrer les dangers propres des divers explosifs et de transporter ceux-ci en toute sécurité.

L'unification des prescriptions sur l'emballage serait aisée à réaliser et il y a lieu de la signaler à la sollicitude des Gouvernements.

Cela dit, voici les trois groupes d'épreuves dont la Commission croit pouvoir recommander l'adoption internationale:

La première épreuve est applicable à tous les types d'explosifs et permettrait de reconnaître immédiatement les produits dont le transport offrirait des dangers; les épreuves suivantes, en précisant les qualités de résistance au choc, à la friction et au feu (à divers degrés), conduiraient à une classification simplifiée des explosifs d'après leurs propriétés.

I.—EPREUVE PRÉALABLE[1]

Deux échantillons, chacun de dix grammes d'explosif non desséche, sont disposés dans des capsules de verre, munies d'un couvercle simplement posé, de 35 millimètres de diamètre et 50 millimètres de hauteur: ils sont introduits dans une étuve chauffée à 75° où ils séjournent pendant 48 heures. On s'assure qu'il n'y a aucune décomposition de l'explosif ni aucune modification notable dans l'aspect ou dans l'odeur. Pour les explosifs nitrés, ils ne doit y doit y avoir auçun degagement de vapeurs rutilantes.

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[1] Voir au procès-verbal de la séance du 24 juin 1912 (annexe VI), les raisons qui ont fait donner à cette première épreuve le nom d'épreuve *préalable* au lieu du nom d'épreuve *d'élimination* qui avait été proposé.

II.—EPREUVE DE RÉSISTANCE AU CHOC

On essaiera des poids égaux de l'explosif à expériménter, préalablement pulvérisé et desséché, d'une part, et d'acide picrique pur pulvérisé et sec, d'autre part, avec le même appareil et dans des conditions identiques. Les prises d'essai, de 5 à 10 centigrammes chacune, seront disposées sur une enclume en acier en une couche occupant $1^{cm}27$ ($\frac{1}{2}$ pouce anglais) *de diamètre. L'explosif est recouvert d'un cylindre en acier trempé, de* $1^{cm}27$ *de diamètre et de même hauteur. Dix essais consecutifs seront exécutes avec chacun des explosifs et serviront à déterminer la hauteur de chute moyenne qui provoque l'explosion.*

Les explosifs considérés comme peu sensibles au choc doivent montrer une insensibilité au moins égale à celle de l'acide picrique pur pulvérisé.

N. B.—Peuvent être notamment employés pour cet essai soit l'appareil anglais à chute libre, soit les appareils décrits au VI^e Congrès international de Chimie appliquée (Rome 1906).

Il est à remarquer qu'ainsi que pour l'épreuve suivante, le mode d'opérer ne doit pas nécessairement être rigoureusement uniforme; la constance des résultats est assurée par l'emploi de l'explosif de comparaison, dans l'espèce l'acide picrique, qui doit être, en tout cas, traité dans le même appareil et de façon rigoureusement la même que l'explosif essayé.

II bis.—EPREUVE DE RÉSISTANCE A LA FRICTION

L'explosif, placé dans un mortier en biscuit légèrement chauffé (20 à 30° centigrades), ne doit pas se montrer moins résistant à la friction que l'acide picrique pur pulvérisé soumis dans le même appareil à une expérience identique.

III.—EPREUVE DE RÉSISTANCE AU FEU

a) EPREUVE A LA MÊCHE: *3 grammes d'explosif pulvérulent sont versés dans un tube-éprouvette en verre: par de légers chocs, on donne à la substance une surface bien unie. On y introduit alors une mèche de poudre brûlant lentement (1 centimètre par seconde). L'essai est répété deux fois:* l'inflammation caractérise les poudre déflagrantes et les explosifs facilement inflammables.

b) EPREUVE SUR UNE CAPSULE DE FER PORTÉE AU ROUGE: Les explosifs ayant supporté l'essai précédent sans déflagration seront soumis à un essai à haute température pour s'assurer de leur inaptitude à la détonation sous l'action du feu.

Une capsule en fer, hémisphérique, de 12 centimètres de diamètre, 1 millimètre d'épaisseur, est portée au rouge sur un brûleur; on y verse d'abord une petite quantité (0.5 gr.) de la substance pulvérisée, puis, s'il ne survient pas de détonation, on augmente la quantité jusque 5 grammes. L'épreuve est recommencée trois fois.

c) L'EPREUVE AU FER ROUGE a pour but de constater l'inaptitude des explosifs de sûreté à l'inflammation.

Apres quelques essais préliminaires sur de petites quantités pour constater d'abord le peu d'inflammabilité relative du produit, on dispose 100 grammes d'explosif sur un carton d'amiante; on met en contact avec l'explosif l'extrémité d'une barre de fer de 15 millimètres de diamètre, portée au rouge cerise (900° environ) sur 10 centimètres de longueur. La matière peut brûler lentement, sans donner lieu à aucune explosion, et doit s'éteindre lorsqu'on retire la source de chaleur.

La conséquence des trois groupes d'épreuves préconisés par la Commission est la répartition des explosifs en trois classes:

Les explosifs sensibles au choc donneront à l'épreuve II–II *bis* des résultats inférieurs à ceux de l'acide picrique et formeront une *première classe* (dynamites, certains explosifs au chlorate et explosifs assimilables).

L'épreuve III *a* caractérisera une *deuxième classe:* les explosifs déflagrant sous l'action de la mèche ou facilement inflammables (notamment les poudres déflagrantes diverses).

L'épreuve combinée III *b* et *c* caractérisera une *troisième classe:* les explosifs insensibles au choc et au feu, dont le transport offre une sécurité presque absolue.

Si certains explosifs, après avoir subi avec succès l'épreuve II–II *bis* et III *a*, détonaient à l'essai de la capsule rougie (III *b*), il faudrait les adjoindre à la *1^re^ classe.* Mais cette éventualité semble ne devoir se recontrer que pour quelques types peu courants.

Les explosifs qui, ayant subi les épreuves II–II *bis*, III *a* et III *b*, se montreraient, dans l'essai III *c*, susceptibles de brûler avec une certaine violence, devraient être rangés dans la 2^e classe (poudres) ou former une sous-classe intermédiaire entre la deuxième et la troisième.

La Commission, en présentant les conclusions qui précèdent au VIII^{me} Congrès international de chimie appliquée, déclare sa mission d'études terminée; elle prie le Congrès d'émettre un vœu à transmettre aux divers gouvernements intéressés, en vue de la réunion d'une convention internationale, munie de pouvoirs officiels, à laquelle il incombera d'achever l'œuvre commencée, en consacrant un accord international sur les questions connexes aux transports internationaux d'explosifs (épreuves, emballage, classification, etc.).

Pour la Commission:

Le Secrétaire,
AD. BREYRE.

Le Président,
V. WATTEYNE.

ANNEXE I

Lettre-circulaire du 12 mars 1912 portant à la connaissance des membres de la Commission, les observations de MM. Bichel, Heise Will, Mente et Lenze et formulant un Avant-Projet de Conclusions

Bruxelles, rue Lambermont, 2, le 12 mars 1912.

Monsieur et honoré Collègue,

Lors du VII^e Congrès international de Chimie appliquée tenu à Londres en 1909, notre Commission a jugé qu'il était utile d'attendre les résultats donnés par l'application du nouveau règlement allemand, en date du 23 décembre 1908, afin de se prononcer en meilleure connaissance de cause sur les épreuves de stabilité dont il conviendrait de recommander l'adoption.

Par nos lettres en dates du 2 février 1911 et du 25 septembre 1911, nous avons prié nos collègues d'Allemagne de nous faire connaître les observations auxquelles donnait lieu, de leur part l'application du règlement nouveau. Ces collègues nous ont fait parvenir les notes suivantes:

NOTE DE M. BICHEL (29 SEPTEMBRE 1911)

J'ai l'honneur de vous accuser réception de vos honorées lettres du 2 février dernier et du 25 courant, et, en réponse, je me permets de soumettre à votre haute compétence quelques points qui, à mon avis, méritent d'être considérés de très près.

Le nouveau règlement relatif au transport, en Allemagne, des explosifs par chemin de fer, n'a pas donné satisfaction à tous les points de vue.

Pour ce qui concerne, par example, la *classification* des explosifs, il est à remarquer que les explosifs à base de chlorate et ceux à base de perchlorate sont traités tous deux sur le même pied, bien que les explosifs à base de chlorate soient de beaucoup plus dangereux que ceux à base de perchlorate.

Autre vice de classification:

D'après le règlement, sont énumérés sous la classe I *a*, groupe 2, des explosifs qui, pour pouvoir voyager à titre de marchandise ordinaire ou de colis, ne doivent pas excéder la quantité de 200 kilos (poids net) à la fois, et qui, expédiés en quantités supérieures à cette limite de 200 kilos, sont classés et rangés sur le même pied que les explosifs du groupe 3, qui sont des explosifs à haut pourcentage en nitroglycérine.

Sous la division *b* sont classés ensuite les explosifs à haut pourcentage en nitroglycérine.

Or cette classification ne pourra guère donner satisfaction aux exigences de la pratique, qui demande plus de latitude. Voyez ce qui se passe tous les jours: les petites stations, au voisinage desquelles se trouvent la plupart des usines des fabricants d'explosifs, ne mettent à la disposition du public qu'un seul wagon par jour pour l'expédition des colis ou de la marchandise ordinaire, de sorte que, vu la restriction précitée, il est impossible aux fabricants d'explosifs d'expédier leurs produits au fur et à mesure des demandes de la journée.

Il faut donc porter la limite de 200 kilos à 500 kilos au moins (poids net), pour sortir de l'embarras et pour concéder aux exigences de la pratique ce qu'on ne peut leur refuser. L'on pourrait faire cette concession sans scrupule et d'autant plus que les explosifs à base de chlorate ne pourront à mon avis, être traités sur le même pied que les explosifs à base de perchlorate qui, fait bien connu, sont beaucoup moins sensibles aux coups, aux chocs et aux causes d'inflammation que les explosifs au chlorate.

NOTE DE M. HEISE (28 OCTOBRE 1911)

Répondant à votre lettre du 25 septembre, j'ai l'honneur de vous informer que j'ai peu à m'occuper de l'application des mesures à prendre pour l'expédition des explosifs. Je n'ai donc pas pu acquérir d'expérience personnelle sur les résultats obtenus avec les nouvelles prescriptions des chemins de fer allemands pour l'essai des explosifs dont il s'agit d'autoriser l'expédition par chemin de fer.

J'ai cherché à obtenir des renseignements à ce sujet, mais n'ai pu arriver à aucun résultat positif, d'autant plus que les fabricants d'explosifs eux-mêmes semblent ne pas encore connaître exactement comment doivent être appliquées ces prescriptions.

A ma connaissance, on n'a eu à déplorer, depuis l'établissement de ces prescriptions, aucun accident lors de l'expédition d'explosifs sur les chemins de fer allemands. Dans quelle mesure cette absence d'accidents est-elle attribuable à l'observation de ces prescriptions, c'est naturellement, ce qu'il est impossible de savoir.

Parmi les membres allemands de la Commission, il y en a quelques-uns qui appartiennent à l'industrie des explosifs. Sans aucun doute, ce sont ceux-ci qui sont le mieux à même de juger des résultats dela nouvelle réglementation. Ils pourront surtout émettre une opinion sur le point de savoir si les nouveaux essais prescrits sont d'exécution facile et d'application pratique.

Supposant que vous pourrez obtenir de ce côté les renseignements concernant les résultats pratiques des nouvelles prescriptions, je me contenterai ici d'inister sur un point concernant le texte même de ces prescriptions.

A mon avis, les prescriptions allemandes ne permettent pas de distinguer exactement dans quels cas il faut procéder aux essais prescrits pour les divers groupes d'explosifs. Les fabricants eux-mêmes semblent être dans le doute à ce sujet.

En tous cas, l'esprit est celui-ci: avant d'admettre au transport un explosif quelconque, ou doit avoir acquis, par suite de nombreux essais, la preuve que cet explosif présente un degré suffisant de sécurité. Dés que l'explosif a satisfait à cet examen, il est, une fois pour toutes, admis au transport par chemin de fer, soit comme marchandise ordinaire, soit seulement par chargements en wagons spéciaux.

Le texte des prescriptions ne cadre pas exactement avec cet esprit. Quelques exemples feront comprendre ma pensée:

Si une firme veut faire admettre au transport un nouvel explosif au nitrate d'ammoniaque, il lui suffit en tous cas de faire une fois les essais prescrits sous la rubrique *I* du chapitre *A* de l'annexe *C1a* du règlement. Ces essais déterminent si, par sa composition et par sa fabrication, le nouvel explosif présente le degré de sécurité nécessaire. Le cas échéant, l'explosif en question sera porté, sous son nom et avec mention de sa composition, dans la liste (annexe *C*) et il sera dès lors admis, n'importe quand, et sans avoir à subir de nouveaux essais, au transport par chemin de fer.

Il en est autrement pour les prescriptions de la rubrique IV concernant les nitrocelluloses (coton-poudre, coton-collodion). Ces explosifs sont admis, d'après les règlements des chemins de fer, sous leurs diverses formes commerciales, à la seule condition qu'ils possèdent un degré suffisant de stabilité. On est donc dans le doute sur le point de savoir quand, dans quels cas ou dans quelles circonstances spéciales, il faut procéder aux essais prescrits, qui ne se bornent pas du tout à rechercher le degré de stabilité. On pourrait admettre que les essais doivent se faire plus souvent. D'ailleurs, ainsi qu'il en est pour d'autres prescriptions concernant d'autres groupes d'explosifs, on ne dit pas toujours à quelles exigences les explosifs doivent satisfaire lors des essais.

Finalement, je voudrais signaler les prescriptions du paragraphe *B* (poudres à tirer) I et II concernant les poudres à la nitrocellulose. Ici, les épreuves doivent s'étendre également aux composants de l'explosif. C'est ainsi, par exemple, que la nitroglycérine doit être expérimentée de deux façons différentes en vue de s'assurer si elle est libre d'acide; or, il est évident qu'une usine peut produire de la nitroglycérine libre d'acide. L'épreuve unique exigée pour l'admission au transport par chemin de fer semble, en conséquence être sans but. Il faut donc comprendre que les prescriptions exigent un examen continuel de la bonne composition des constituants, car l'accomplissement des prescriptions n'a pas seulement pour but de faire observer une forme extérieure, mais il vise aussi à arriver à ce résultat qu'on n'admette au transport par chemin de fer que des explosifs de mine ou de tir présentant réellement un degré de sécurité déterminé.

Si donc la Commission voulait reprendre les prescriptions allemandes, je proposerais de diviser les essais en deux classes:

1° Essais pouvant fournir la preuve qu'un nouvel explosif possède le degré de sécurité nécessaire pour être admis au transport par chemin de fer;

2° Essais pouvant prouver la sécurité de chaque envoi en particulier.

Les essais prévus au 1° ne devront avoir lieu qu'une fois; de plus, à chaque expédition, il faudra que la lettre de voiture porte une mention d'un chimiste agréé par l'administration, attestant que l'explosif expédié est le même que l'explosif admis.

Les essais prévus au 2° ne pourront être exigés que pour les explosifs qui, ou bien n'auraient pas satisfait aux essais prévus au 1°, ou pour lesquels ces essais ne donneraient pas suffisamment de garanties.

NOTE DE MM. WILL, MENTE ET LENZE (7 NOVEMBRE 1911)

En général, on se trouve bien des prescriptions allemandes concernant les explosifs à admettre au transport par chemin de fer. Elles sont maintenant en usage depuis deux ans et nous pouvons recommander de les prendre pour base des conventions internationales.

Tout d'abord, on parait satisfait du principe qui consiste à admettre au transport d'après les résultats d'un essai expérimental détaillé effectué suivant des prescriptions déterminées. Les exigences auxquelles les explosifs doivent satisfaire ont été fixées en s'inspirant autant que possible des nécessités de l'industrie et avec la collaboration des fabricants d'explosifs, tout en tenant compte du degré de sécurité nécessaire pour le transport par chemin de fer. On est d'accord pour trouver bon le principe de procéder aux essais en prenant comme terme de comparaison un explosif approprié.

Il nous semble que certains changements de détail mériteraient d'être considérés.

On se demande s'il ne serait pas possible de trouver un explosif de comparaison répondant mieux que la *Donarite* au but proposé pour le groupe des explosifs au nitrate d'ammoniaque. Cet explosif devrait avoir une composition plus simple et, au point de vue de certaines prescriptions des essais, satisfaire à des exigences moindres. Il nous semble qu'avec la Donarite comme explosif de comparaison, on arrive à des exigences trop sévères pour ce qui concerne l'épreuve d'inflammation dans le récipient en tôle et peut-être aussi l'épreuve de déflagration.

Il faudrait aussi examiner si l'épreuve de résistance dans un dépôt chauffé à 75°, épreuve qui, actuellement, ne dure que 48 heures, ne devrait pas avoir sa durée augmentée jusque huit jours. Tous les explosifs au nitrate d'ammoniaque fabriqués actuellement en Allemagne passent très facilement cette épreuve, et les quelques explosifs qui furent présentés jadis et ne réussirent pas à passer cette épreuve, sans se décomposer, montsèrent qu'on ne pouvait pas avoir en eux entière confiance. Il faut donc que le "standard" de ces essais ne soit pas placé trop bas, surtout qu'il arrive souvent que les explosifs, sans qu'il soit possible de les emballer de nouveau, doivent être aussi admis au transport sur navires marchands.

On se demande aussi s'il ne serait pas convenable, maintenant que, depuis l'introduction de la nouvelle règlementation des chemins de fer, on a à sa disposition un matériel très considérable pour juger des propriétés des divers groupes d'explosifs, d'essayer de remplacer par un groupement plus général la si grande spécialisation dans la composition des explosifs et l'énumération de chaque explosif en particulier (par exemple du groupe I), comme il était nécessaire de le faire avant que l'expérience que nous possédons actuellement ne fût acquise. Il y aura à voir s'il ne conviendrait pas de faire à ce sujet une proposition plus précise d'ici à la date du prochain Congrès international.

Les prescriptions des essais ont été interprétées dans la pratique par l'Administration des chemins de fer en ce sens que l'on range, au point de vue de leur admission au transport, les explosifs genre poudre noire, d'un maniement sans danger, dans le groupe I, et ceux du genre des explosifs au chlorate et au perchlorate dans le groupe II. Cette classification a été faite à la suite d'un essai d'incendie en grand (respectivement 500 et 200 kilogrammes d'explosifs emballés règlementairement). On se demande si on ne pourrait, en le modifiant, rendre plus simple cet essai considérable et, en tous cas, coûteux. Ici aussi, on a déjà, par exemple pour les poudres noires de maniement peu dangereux, des essais parallèles dans des caisses en tôle, mais on n'a pas encore définitivement pris position au sujet de ces essais.

Pour les conventions internationales on devrait désigner comme explosif de comparaison pour l'essai des munitions de tir de groupe B, une poudre que l'on puisse se procurer partout.

OBSERVATIONS RELATIVES AUX NOTES PRÉCÉDENTES ET NOTRE AVANT-PROJET DE CONCLUSIONS

Les critiques de M. Bichel relatives au poids maximum d'explosifs du groupe II qui peut être transporté comme marchandise ordinaire, ne sont pas du ressort de la Commission internationale: ce sont là des points de pratique administrative, spéciaux à chaque pays, où notre Commission n'a pas à s'immiscer.

Il en est autrement de l'observation judicieuse de M. Bichel critiquant la mise sur le même pied des explosifs à base de chlorate et de perchlorate, alors que les seconds sont beaucoup moins dangereux que les premiers; il y a là une de ces inconséquences auxquelles aboutissent tous les essais de classification chimique des explosifs, alors que seul le groupement d'après un ensemble de propriétés reconnues est désirable. Nous reviendrons sur ce point plus loin.

M. le Professeur Heise émet quelques critiques tendant à voir préciser quand les essais sont obligatoires pour chaque groupe d'explosifs; il voudrait voir distinguer les essais de reconnaissance de ceux qui, dans certains cas, devront accompagner les expéditions d'explosifs.

La note collective de MM. Lenze, Mente et Will résume en ses grandes lignes le résultat du nouveau règlement allemand et suggère divers perfectionnements qui leur paraissent désirables.

Il vous appartient, très honoré Collègue, de formuler toutes observations qui vous paraîtraient opportunes sur les points soulevés par Messieurs nos Collègues d'Allemagne.

Mais pour hâter le plus possible les travaux de notre Commission et permettre de présenter des conclusions au prochain

Congrès, nous croyons devoir vous soumettre ci—dessous un *avant-projet* indiquant quels pourraient être la *classification* et les *épreuves de stabilité* qui feraient l'objet de conventions internationales.

En rédigeant cet avant-projet, nous sommes partis des principes exposés, dans le précédent rapport, au Congrès de Londres, à savoir:

1° Que les explosifs industriels doivent seuls, pour le moment, du moins, être considérés par la Commission;

2° Que les épreuves à adopter internationalement doivent être en petit nombre et aussi simples que possible pour qu'elle puissent toujours être reproduites aisément dans des conditions identiques.

Ajoutons que ce sera déjà un grand point acquis, vu les difficultés du problème, si l'on parvient à se mettre d'accord sur un petit nombre d'épreuves.

La question restera ouverte, et, une fois l'accord établi, ne fût-ce que sur un ou deux points, il s'établira aisément plus tard sur d'autres, au fur et à mesure que la possibilité apparaîtra d'adopter telle ou telle épreuve supplémentaire.

Nous allons donc indiquer d'abord quelle pourrait être, d'après nous, la classification à adopter, puis nous proposerons un nombre restreint d'épreuves en rapport avec cette classification.

1.—CLASSIFICATION

On a vu, par le premier rapport, combien les classifications varient dans les différents pays, sans réussir, par la multiplication des classes, à grouper les mélanges d'égal danger. Cela provient, croyons-nous, de ce que l'on a voulu suivre de trop près la composition chimique des explosifs, alors que le vrai critérium, dans une classification qui vise spécialement l'emmagasinage et le transport, réside dans les propriétés qui traduisent la résistance des produits aux diverses causes de danger.

Il y aurait lieu de proposer une classification simplifiée, basée sur ces propriétés, et qui pourrait être, par exemple, la suivante:

I. *Explosifs plus sensibles au choc, susceptibles de détoner sous l'action du feu*

Dans cette catégorie se rangeraient les dynamites, les nitrocelluloses, les fulminates (généralement exclus de tout transport), les explosifs aux chlorates, les picrates et ceux qui ne pourraient être rangés dans d'autres catégories.

Ces explosifs seraient notamment ceux rentrant dans le cadre ci-dessous indiqué:

a)	Nitroglycérine	20 à 92%
	Nitrocellulose (collodion)	3 à 10 "
	Nitrate d'ammoniaque, de soude, de potasse	5 à 30 "
	Celluloses diverses, farine de seigle, de blé, etc.	5 à 30 "
b)	Chlorate de potasse	70 à 80%
	Dérivés nitrés (nitronaphtaline, nitrotoluène, etc.)	2 à 15 "
	Huile d'enrobement (huile de ricin, résine, etc.)	5 à 10 "

II. *Les explosifs pratiquement insensibles aux chocs mais déflagrant ou brûlant violemment sous l'influence d'une flamme ou d'une élévation brusque de la température*

Cette classe comprendrait la plupart des poudres noires et des poudres sans fumée. Ce seraient les explosifs composés suivant les formules suivantes:

A. *Genre des poudres noires;*

Nitrate de sodium, de potasse, de baryum	70 à 75%
Soufre	8 à 13 "
Charbon de bois, brun, noir, etc	12 à 15 "
Matières inertes diverses	0 à 10 "

B. *Poudres sans fumée;*

Nitrocellulose gélatinisée	0 à 100%
Nitroglycérine gélatinisée	0 à 58 "
Paraffine, vaseline, camphre, etc	0 à 5 "
Nitrate de baryum, de potassium, etc	0 à 25 "

III. *Les explosifs pratiquement insensibles aux chocs et ne brûlant pas ou brûlant lentement sous l'influence d'une flamme*

Cette classe renfermerait la plupart des explosifs au nitrate d'ammoniaque, y compris certains qui renferment du perchlorate. Les explosifs de cette classe seraient, notamment, ceux rentrant dans le cadre suivant:

Dérivés nitrés: Nitrotoluène, nitronaphtaline, nitrobenzine	5 à 15%
Nitrate d'ammoniaque	60 à 90 “
Nitrates, chlorures, chromates, alcalins	20 à 40 “
Celluloses, glucoses, farines diverses, saccharoses, dextrines	4 à 10 “
Nitroglycérine	0 à 6 “
Nitrocellulose	0 à 1 “
Matières grasses, résines, etc.	0 à 6 “
Perchlorate d'ammonium	0 à 40 “

II.—ÉPREUVES

Tout le monde convient qu'il faudrait des épreuves simples et peu nombreuses; il faut, de plus, que ces épreuves puissent se reproduire partout, très facilement, dans des conditions identiques.

C'est pourquoi il nous a paru désirable de limiter les épreuves à trois essais successifs: le premier constituerait une épreuve éliminatoire; faute d'y avoir satisfait, les explosifs seraient exclus de tout transport; c'est un essai de résistance à la chaleur. Un second essai de résistance au choc caractériserait ensuite la classe I (dynamites et matières à y assimiler). Le troisième essai, en déterminant la résistance au feu, isolerait la classe II (poudres déflagrantes) de la classe III.

1° Essai de résistance à la chaleur suivant le mode indiqué dans le règlement allemand, c'est-à-dire par exposition à la température de 75° pendant 48 heures, sans qu'il résulte de diminution de poids ou de décomposition quelconque. La température pour les explosifs à base de nitroglycérine pourrait être abaissée à 50°. Cette épreuve permettra de constater s'ils ont une tendance à l'exsudation. Elle sera combinée à un essai chimique qui consistera à constater que l'explosif n'a pas plus de tendance à rougir le papier de tournesol après l'exposition qu'avant.

2° Une épreuve de résistance au choc par un essai au mouton dans les conditions suivantes qui nous paraissent les plus précises et qui sont la reproduction de l'épreuve usitée en Grande-Bretagne (voir note de M. Lundholm dans les premiers rapports).

L'enclume, en acier, est recouverte d'une mince couche d'explosif (1^{mm}), occupant un cercle de 1 cent. 27 de diamètre; l'explosif est recouvert d'un cylindre en acier durci de 1 cent. 27 de diamètre et de même hauteur; le mouton est constitué par une boule retenue par la pièce polaire sphérique d'un électro-aimant; en interrompant le courant, on provoque la chute de la boule de hauteurs règlables.

Suivant la hauteur nécessaire pour amener la détonation de l'explosif, la matière examinée rentrerait dans la catégorie I (faible hauteur de chute) ou dans l'une des catégories II et III.

C'est pour spécifier dans laquelle de ces deux dernières catégories l'explosif devrait être classé que serait fait l'essai suivant:

3° Essai de résistance au feu. Cette épreuve ne vise pas la détermination dela températre d'inflammation mais simplement le degré de danger que tel ou tel explosif peut présenter dans le transport. Un essai d'inflammation à la mêche ou à un bec Bunsen suffira immédiatement pour caractériser la classe II (poudres déflagrantes).

Pour l'admission à la classe III, l'essai qui nous paraît unir au maximum de simplicité une exactitude suffisante est celui du fer rouge: après quelques essais préliminaires sur de petites quantités pour constater d'abord le peu d'inflammabilité relative du produit, on introduit un fer rouge dans une cartouche de 100 grammes entourée de son enveloppe; la matière peut brûler lentement, sans donner lieu à aucune explosion, et doit s'éteindre lorsque l'on retire la source de chaleur.

Ces essais pourraient, naturellement, être toujours exigés par l'administration compétente du pays où entrent les transports d'explosifs. Chaque envoi serait accompagné d'un certificat du directeur de l'usine indiquant la composition de l'explosif et attestant qu'il a subi les épreuves de classement. Sur le vu de cette pièce, l'administration compétente pourrait ne pas exiger 'lexécution de ces essais.

On objectera peut-être au premier essai qu'il est trop rigoureux pour les nitrocelluloses. Si vous le jugez ainsi, vous pourriez proposer une autre épreuve équivalente pour ces composés. Remarquons d'ailleurs que les nitrocelluloses ont une très minime importance dans les explosifs industriels, les composés qui les renferment étant tous des explosifs de tir dont, pour les motifs déjà indiqués, la Commission croit ne pas devoir s'occuper.

Nous vous saurions gré, Monsieur et Honoré Collègue, de nous faire parvenir avant le 15 avril les observations que suggère la solution que nous avons esquissée plus haut. Après examen de ces observations, nous pourrons procéder à l'élaboration d'un rapport définitif.

Quelques collègues ont proposé, vu l'éloignement du prochain Congrès et l'impossibilité dans laquelle plusieurs d'entre nous pourront se trouver de se rendre en Amérique, de nous réunir en mai ou au commencement de juin dans une ville d'Europe,—Paris, par exemple, ou ailleurs,—en vue de nous concerter et d'arriver à un accord définitif.

Veuillez nous dire si vous approuvez ce projet, quelle ville vous proposez et quel jour—approximativement—vous conviendrait.

Mais pour que cette réunion soit efficace, il importe que, bien avant la date choisie, vos observations sur le rapport ci-dessus esquissé nous aient été envoyées, de telle sorte qu'un projet définitif puisse être discuté et adopté.

Agréez, Monsieur et honoré Collègue, l'assurance de notre considération la plus distinguée.

Le Secretaire, *Le President,*
AD. BREYRE. V. WATTEYNE.

ANNEXE II

Lettre-circulaire du 18 mai 1912 contenant les observations de MM. Will, Mente et Lenze, Heise, Barthélemy, Jacqué et Lundholm

Monsieur et Honoré Collègue,

Notre lettre-circulaire du 12 mars dernier signalait l'utilité d'une réunion de notre Commission fin mai ou au commencement de juin; la majorité de nos Collègues ont désigné Paris comme lieu de réunion et M. Barthélemy veut bien mettre ses bureaux à notre disposition.

Nous avons donc fixé cette réunion à Paris, au lundi 24 juin prochain, dans les bureaux de M. Barthélemy, 66, chaussée d'Antin (*Société française des pourdes de sûreté*). Une première séance aura lieu à 10 heures du matin; elle sera reprise, si besoin en est, à 3 heures de l'après-midi.

Pour hâter et faciliter la discussion, nous croyons utile de vous faire connaître les observations qui nous sont parvenues à la suite des propositions contenues dans notre lettre-circulaire rappelée ci-dessus.

NOTE DE M. WILL

Neubabelsberg, le 15 avril 1912.

Après conférence avec MM. Mente et Lenze d'accord entre nous, nous avons l'honneur de répondre à votre lettre du 12 mars ce qui suit:

Nous nous sommes d'abord occupés des lettres de M. Bichel et de M. Heise. Pour ce qui concerne les dires de M. Bichel au sujet du danger que présentent les explosifs au chlorate et ceux au perchlorate, il faut convenir qu'en général, les perchlorates, comme éléments constituants d'explosifs, doivent être regardés comme étant moins dangereux que les chlorates. Cependant, il résulte des expériences dont nous avons examiné les résultats, que les mélanges au perchlorate en question se placent, au point de vue de leur sensibilité et de leur tendance à exploser, entre les mélanges analogues au chlorate et ceux au salpêtre; mais, au point de vue de leurs propriétés, ils se rapprochent davantage des explosifs au chlorate que de ceux au salpêtre, et lorsqu'on a procédé à la division des explosifs en classes suivant le degré de danger qu'ils présentent, on a été d'avis que la différence de sensibilité entre les explosifs au chlorate et ceux au perchlorate ne justifiait pas la classification de ces deux sortes d'explosifs en deux classes distinctes.

Pour ce qui concerne la question d'expédition en charges de 200 ou de 500 kil. à la fois, nous partageons votre avis que c'est là un point à régler par chaque pays séparément.

Concernant la lettre de M. Heise, il nous paraît exister un malentendu. Le règlement allemand n°. 1 pour le transport par chemin de fer, (annexe *C1a*), prescrit que pour chaque expédition il doit être fourni une preuve d'accomplissement des essais devant décider si l'explosif est ou non admissible au transport par chemin de fer.

On a eu suffisamment de confiance dans l'industrie pour trouver inutile de faire contrôler cette preuve chaque fois par l'Administration et, jusqu'à présent, on n'a pas à regretter cette confiance.

Les attaques contre l'exigence d'un essai de la nitroglycérine servant à la fabrication des poudres ne nous paraissent pas non plus justifiées. Il paraît, en effet, raisonnable d'attirer l'attention des fabricants sur ce fait qu'une poudre à admettre au transport par chemin de fer ne doit être fabriquée qu'avec une nitroglycérine bien stable, et, par conséquent, l'épreuve exigée doit se faire dans la fabrique d'une façon sérieuse.

Quant aux propositions de M. Heise pour le cas où la Commission internationale adopterait le règlement allemand, on peut les accepter d'autant mieux que, pour chaque expédition, la prescription citée plus haut exige une attestation concernant également l'emballage.

Finalement, pour ce qui concerne votre proposition d'une nouvelle classification des explosifs à admettre au transport par chemin de fer, nous devons dire qu'elle nous plaît par sa simplicité; on nous permettra cependant de remarquer que, lors du premier essai de rédaction du règlement allemand, c'est de ce principe qu'on est parti en première ligne. Ce n'est qu'en classifiant les explosifs qu'on a reconnu l'avantage ou la nécessité de diviser davantage, en partie en considération des exigences, reconnues fondées, du service de transport. Nous craignons que, lorsqu'on se mettra à vouloir faire entrer dans les catégorie proposées par vous tous les explosifs, on ne se heurte de nouveau à de pareilles difficultés.

Nous reconnaissons néanmoins, et, en cela, confirmons nos remarques précédentes, que, en certaines parties, notre règlement pour le transport par chemin de fer, annexe C, est encore susceptible de simplification, surtout dans la partie concernant le groupe I; mais, jusqu'à présent, il ne nous a pas été possible de procéder à cette simplification, le matériel expérimental à notre disposition étant insuffisant.

Agréez, etc.

II.—NOTE DE M. HEISE

Boçhum, le 9 avril 1912.

Les propositions faites par votre lettre du 12 mars dernier concernant la division en classes des explosifs et les essais auxquels ces explosifs devraient être soumis pour être admis au transport par chemin de fer, diffèrent très sensiblement des prescriptions allemandes. Le point de vue auquel vous vous placez ne me semble cependant pas injustifié. Notre règlement allemand, outre que sa rédaction est défectueuse à mon avis, est beaucoup trop sévère et part d'un point de vue trop peu général pour qu'il puisse être pris comme base d'une entente internationale.

Dans votre lettre, vous désirez diviser les explosifs en trois classes; de même, l'examen que devrait subir chaque explosif ne comprendrait essentiellement que trois épreuves. Cette simplification constituerait un progrès notable.

La Commission internationale doit restreindre son action aux "explosifs industriels," cela veut dire, sans doute, les explosifs employés dans les exploitations industrielles telles que mines, minières, carrières, par opposition aux explosifs de tir et de guerre. Cependant, nous voyons figurer en groupe séparé les poudres sans fumée qui, pourtant, ne sont utilisées, en pratique, que pour le tir.

On propose donc de diviser les explosifs en trois classes:

CLASSE I.—Explosifs très sensibles aux chocs et au feu.

CLASSE II.—Explosifs peu sensibles aux chocs mais très sensibles au feu.

CLASSE III.—Explosifs peu sensibles aux chocs et au feu.

Cette division est basée sur les dangers auxquels les explosifs peuvent être exposés au cours de leur transport en chemin de fer. Nous présumons que ces dangers comprennent les collisions et déraillements (choc) ainsi que l'incendie (feu). Comme il peut difficilement être question d'autres dangers, on peut approuver la division proposée; on peut se demander pourtant comment, en pratique, on réalisera cette division en trois classes.

Vous parlez de trois épreuves différentes auxquelles les explosifs devraient successivement satisfaire. D'après les résultats de ces épreuves on déciderait d'abord si l'explosif peut être admis au transport par chemin de fer; suivant les résultats des deux autres épreuves, l'explosif serait classé dans l'une ou l'autre des trois catégories.

L'épreuve n°. 1 consiste à exposer l'explosif pendant 48 heures à une température de 75° C; au cours de cette épreuve, il ne doit ni se décomposer ni diminuer de poids. Cette température de 75° serait réduite, pour les explosifs à la nitroglycérine, à 50°. De plus, après cette épreuve, les explosifs ne doivent pas avoir plus de tendances à teinter le papier tournesol qu'avant.

L'épreuve n° 2 est celle du mouton à la manière anglaise.

L'épreuve n° 3 consiste à examiner la manière de se comporter de l'explosif en présence du feu (avec mèche, bec Bunsen, fer rouge).

Supposons qu'un explosif a satisfait à l'épreuve n° 1. A l'épreuve n° 2 (mouton), il détone sous le choc d'un boulet de 0.5 kil. tombant d'une hauteur de $0^{m}20$. A l'épreuve n° 3, il s'enflamme, quoique difficilement, au contact d'une flamme de Bunsen. On peut obtenir ces résultats, par exemple, avec la *Nobelite* ou la *Gélatine carbonite.* Dans quelle classe ranger un tel explosif? Pas dans la classe III, puisqu'il s'enflamme au contact d'une flamme Bunsen: dans la classe I ou dans la classe II? Il est impossible de le dire. L'épreuve du mouton manque d'un "standard." Si on veut que cette épreuve soit utile, il faut ou bien fixer pour chaque classe une certaine hauteur de chute jusque ou en-dessous de laquelle l'explosif ne doit pas détoner (naturellement, le poids du mouton serait aussi déterminé), ou bien il faut faire appel, pour chaque classe, à la comparaison avec un explosif type. A mon avis, ce dernier procédé serait le meilleur.

Sous ces réserves, la division proposée des explosifs en trois classes serait peut-être possible.

Par contre, je ne suis pas partisan du principe, tel qu'il se trouve en annexe, d'établir des distinctions basées sur la composition chimique. Prenons, par exemple, la classe I; les compositions chimiques y citées ne s'appliqueraient pas à la carbonite, celle-ci contenant plus de 30% de farine. De plus il n'est pas possible de n'admettre dans la classe II que la poudre noire et les poudres sans fumée; la dénomination même de "poudres déflagrantes" pour la classe II couvrirait encore un champ trop restreint. Il est, en effet, très possible que les résultats de l'épreuve n° 2 (inflammation par mèche ou par Bunsen)feraient admettre dans cette classe maints explosifs au perchlorate ou au nitrate d'ammoniaque (par exemple, ceux contenant une forte proportion d'aluminium). Pour ranger les explosifs dans le trois catégories proposées, il ne faut se baser que sur les résultats des trois épreuves en question.

Pour ce qui concerne ces épreuves elles-mêmes, on ne pourrait objecter contre l'épreuve n° 1 que sa sévérité, peutêtre excessive, pour les nitrocelluloses. Il est vrai que ces explosifs sont fort peu employés dans l'industrie. Il faudrait cependant, pour l'exécution de cette épreuve, édicter des prescriptions supplémentaires (composition de l'explosif avant l'épreuve, quantités d'explosifs, etc.) plus ou moins comme le règlement allemand, aux paragraphes 1–3.

L'épreuve n° 2 à pour but de sélectionner les explosifs à admettre dans la classe I. On pourrait peut-être, objecter que l'épreuve du mouton ne donne pas de résultats exacts. Cependant, le règlement allemand, lui aussi, attache à cette épreuve une grande importance; mais l'emploi de la manière anglaise constitue un progrès, en ce sens que la chute du boulet est provoquée par l'action d'un électro-aimant. Pour le reste, il faudrait encore, pour cette épreuve, entrer dans plus de détails (poids du boulet, température à laquelle se fait l'essai, nombre des essais, détonation complète ou partielle), comme les mentionne le règlement allemand sous la rubrique I 6 *a*.

L'épreuve n° 3 paraît, à première vue, très simple. Il faudrait cependant que les conditions en soient également exactement déterminées. Avec la mèche, il n'est même pas toujours possible d'enflammer la gélatine dynamite; presque jamais on n'arrive à enflammer les nouveaux explosifs de sûreté contenant 20 à 30% de nitroglycérine. Par contre, une flamme de Bunsen enflammera presque tous les explosifs, même la plupart de ceux au nitrate d'ammoniaque; il est vrai qu'une partie d'entre eux s'éteindra lorsqu'on retirera la flamme du Bunsen. Quoi qu'il en soit, il vaudrait mieux classer dans cette catégorie les explosifs qui, au contact d'une flamme de Bunsen, non seulement s'enflamment mais continuent de brûler une fois retirée la source de chaleur. D'ailleurs, en pratique, cette épreuve ne pourrait s'appliquer qu'aux explosifs qui, d'après les résultats de l'épreuve n° 2, seraient déjà à ranger dans la classe III.

En résumé, je suis partisan de vos propositions, mais aussi, de l'introduction d'explosifs de comparaison aussi simples que possible, ce qui permettrait de mettre en limière les différences inévitables entre les résultats des essais.

Agréez, etc.

III.—Note de M. Barthélemy

Paris, le 27 avril 1912.

J'ai l'honneur de vous informer que les personnes compétentes que j'ai consultées ne font qu'une seule objection au mode d'épreuve de résistance à la chaleur que vous proposez: on trouve qu'un essai de 48 heures à 50° est insuffisant parce qu'il peut très bien se faire que, dans le midi de la France ou en Algérie, des explosifs se trouvent soumis dans des wagons fermés pendant plus de 48 heures à une température voisine de 50°. On pense généralement que l'essai de résistance à la chaleur devrait être au moins de quatre jours à 75° ou de huit jours à 50°.

A part cela, votre projet de classification et d'épreuves simplifiées ne peut être qu'approuvé.

Veuillez agréer, etc.

IV.—Note de M. Jacqué

La Cantabrica, le 6 avril 1912.

Quoique les règlements allemands concernant les explosifs paraissent satisfaisants dans leur ensemble, il serait assez difficile de les faire accepter d'une façon absolue dans tous les pays sans leur faire subir des modifications de détail, dans le but de simplifier les épreuves imposées et de faciliter les conditions de transport, sans causer d'ailleurs le moindre préjudice soit aux Compagnies de transport, soit au public en général. Ces modifications sont de deux ordres: les premières se rapportent aux épreuves d'admission des explosifs et au classement qui en résulte; les secondes ont trait aux conditions de transport.

DES ÉPREUVES ET DU CLASSEMENT DES EXPLOSIFS

Tout d'abord, le principe d'après lequel les explosifs ne doivent être admis au transport que lorsque leur composition et leurs propriétés sont bien connues et ont fait l'objet d'essais détaillés n'est pas discutable. Tout le monde est aussi d'accord pour reconnaître que le meilleur moyen de classement consisterait à comparer l'explosif examiné avec quatre ou cinq types bien étudiés, dont l'inflammabilité, les sensibilités au choc, à la friction, la susceptibilité de faire explosion dans des conditions variées (masse, explosion à l'air libre ou en vase clos, sous l'influence de détonateurs de plus en plus actifs, etc. . . .) ont été bien déterminées une fois pour toutes. On a ainsi un moyen commode de fixer rapidement à quelle catégorie un explosif nouveau doit être rapporté; sa composition même la détermine presque d'avance et, en tout cas, des essais comparatifs très simples avec les explosifs types vérifieraient rapidement les présomptions.

LA CLASSIFICATION

La classification proposée par notre très honoré Président paraît excellente; je me permettrai cependant de faire remarquer qu'il y aurait peut-être lieu de créer une classe spéciale pour les détonateurs (fulminates et succédanés), ces produits devant toujours être séparés des explosifs proprement dits, pendant le transport des explosifs. D'autre part, il me semble que les règlements sont encore bien sévères pour les nitrocelluloses contenant de 30 à 35% d'eau et de stabilité préalablement reconnue: le transport effectué dans de semblables conditions est moins dangereux que celui de la paille sèche. A mon avis, on devrait, considérer ce genre de matières comme marchandise ordinaire, au moins pour les transports peu lointains. Quant à la nitrocellulose sèche, il est clair qu'il faut la ranger dans la classe des dynamites et des explosifs chloratés avec dérivés nitrés divers et huiles d'enrobement. Dans ce groupe entreraient tous les explosifs qui offrent des dangers analogues à ceux de la dynamite n° 1 au point de vue choc et inflammation, et à ceux d'un type chloraté, qui pourrait être par exemple 85% de chlorate de potasse et 15% de résine, au point de vue friction et choc.

Il est tout à fait plausible de faire une classe à part des diverses poudres du type "poudre noire" et d'y réunir les poudres sans fumée, colloïdales diverses de stabilité éprouvée. Les unes comme les autres ne présentent d'autre danger réel que celui d'inflammation au contact de la flamme.

Quoiqu'elle paraisse bien vaste, la classification, en un seul groupe, des explosifs à base d'hydrocarbures nitrés, nitrates alcalins, chromates avec addition de résines, paraffines, etc., et moins de 6% de nitroglycérine serait bien commode. On ne peut s'empêcher cependant de faire remarquer que, si presque tous les explosifs de cette catégorie sont à peu près exempts de dangers tant au point de vue transport qu'au point de vue emmagasinage, il y en a cependant quelques uns qui sont de véritables explosifs, tandis que d'autres sont tellement insensibles au choc et si difficilement inflammables qu'on se demande pourquoi on leur appliquerait une règlementation spéciale. C'est ici sans doute que la comparaison avec des types d'une insensibilité connue rendrait service pour éliminer de la classification comme explosifs ceux des produits qui n'y figurent que parce que l'on sait d'avance l'emploi auquel ils seront destinés. Tels sont par exemple les explosifs incomplets où la matière combustible (hydrocarbures faiblement nitrés avec addition de très faibles quantités de nitroglycérine et de paraffine, cires, etc,) est transportée indépendamment du comburant.

Au sujet des perchlorates, je suis tout à fait de l'avis de M. Bichel; si l'on ne veut pas en faire une classe spéciale, les explosifs contenant moins de 40% de perchlorate pourraient parfaitement faire partie du groupe III proposé par M. Watteyne. Certains mélanges de perchlorate d'ammoniaque et de nitrate de soude avec des comburants convenablement choisis réunissent toutes les conditions de sécurité, à tous les points de vue, des types les moins sensibles des explosifs du genre Favier. Mais lorsqu'il s'agit d'explosifs chloratés ou perchloratés, il y a toujours lieu de se mettre en garde contre certaines associations qui peuvent devenir dangereuses. Il y a des cas où la connaissance de la composition chimique permet d'opposer un veto absolu à l'admission de certains mélanges en apparence inoffensifs.

LES ÉPREUVES

Si la composition de l'explosif est telle qu'il ne puisse, dans des conditions normales, être susceptible de modifications dangereuses faciles à prévoir, les épreuves auxquelles M. Watteyne propose de soumettre les explosifs nous paraissent tout à fait suffisantes en ce qui concerne la question du transport et de l'emmagasinage.

Il sera bon toutefois d'attirer l'attention sur certaines incompatibilités: par exemple, un explosif contenant du nitrate d'ammoniaque et du chlorate de potasse est dangereux a priori puisqu'il peut se former du chlorate d'ammoniaque, corps qu'il faut autant que possible éviter, à cause de sa grande sensibilité; pour la même raison, on n'admettra pas de mélanges perchlorate d'ammoniaque et chlorate de potasse, etc. Pour des raisons analogues, on n'admettra qu'avec la plus grande prudence des mélanges contenant des picrates ou crésylates d'ammoniaque, de l'acide picrique ou du trinitrocrésol en présence de chlorates. Les nitrates de plomb sont aussi dangereux en présence de picrate de potasse, etc.; le permanganate de potasse et en général les oxydants violents sont suspects en présence de matières cellulosiques finement moulues. Il ne serait peut-être pas inutile de tenir compte de ces incompatibilités puisque des explosifs qui pourraient passer les épreuves, n'en seraient pas moins susceptibles de donner lieu à des surprises désagréables au bout d'un certain temps (Transports lointains).

1° Cela posé, l'essai de chaleur à une température de 50° pendant 48 heures avec examens d'acidité et d'état physique et chimique avant et après l'essai suffira en général à constater la résistance bonne ou mauvaise des explosifs à base de nitroglycérine: quant aux pertes de poids, il ne faudrait pas leur donner une grande importance, si elles sont faibles: elles peuvent être dues en effet à une petite perte d'humidité; cette dernière est toujours notable avec les produits qui contiennent des sels hygroscopiques (nitrate d'ammoniaque, nitrate de soude, perchlorate d'ammoniaque, chlorure de magnésium, etc.) Mais la comparaison des autres épreuves (choc et inflammation) faite sur le produit avant et après dessication guidera toujours convenablement l'observateur. Il suffira, après examen de l'acidité, de s'assurer que la résistance au choc (après refroidissement) et la résistance au feu n'ont varié que d'une façon à peine sensible. Il peut parfois y avoir une très légère variation dûe à un départ d'humidité.

2° Pour l'épreuve de résistance au choc, nous employons aussi de préférence la boule sphérique tombant en chute libre, système qui nous paraît plus rationnel que ceux où la masse pesante est guidée et par conséquent peut être soumise à des frottements imprévus qui modifient les conditions du choc. Un autre procédé, commode dans bien des cas, consiste à essayer l'action de détonateurs successivement croissants sur une cartouche métallique longue et étroite. La quantité de fulminate à employer donne une idée exacte de la sensibilité au choc et de la tendance à la propagation de l'explosion.

3° L'essai au fer rouge, tel que le décrit M. Watteyne, est suffisant pour permettre de ranger un explosif dans la classe III, telle qu'il la définit.

Il ne resterait plus à parler que du cas ou la matiere examinée n'a pas les propriétés explosives qui justifient l'application d'un tarif spécial, mais contient cependant un mélange de matières qui peuvent servir à fabriquer des explosifs. Il semble qu'une fois l'insensibilité au choc et à la friction bien établie, il suffirait de démontrer qu'un incendie entretenu dans une masse de 25 ou 30 kg. du produit peut être aussi facilement éteint que le serait une même quantité de paraffine ou de cire maintenue enflammée dans les mêmes conditions. S'il en est ainsi, nul ne niera que la matière examinée n'est pas réellement un explosif au point de vue transport et emmagasinage.

En résumé, sauf ces quelques petites observations, la classification et les épreuves proposées dans l'avant-projet de notre très honoré Président réunissent à la fois l'exactitude et la simplicité qui, suivant sa très juste remarque, sont indispensables pour que le règlement international projeté puisse être adopté.

CONDITIONS DE TRANSPORT

Je ne crois pas que l'on puisse faire aux conditions de transport telles qu'elles sont ordonnées par le nouveau règlement allemand d'autres objections sérieuses que celles qu'a déjà formulées M. Bichel, à savoir qu'il convient de de faire une distinction entre les explosifs chloratés et les explosifs perchloratés, surtout lorsqu'il s'agit d'explosifs contenant moins de 45% de perchlorates. Il serait équitable qu'on fasse entrer dans le groupe I du règlement allemand (nouveau groupe III de M. Watteyne) ceux de ces explosifs qui satisfont aux conditions de sécurité imposées au dit groupe; tout au moins pourrait-on sans inconvénients élever notablement la quantité d'explosifs de ce genre qui est actuellement autorisée à voyager comme colis avec les marchandises ordinaires. Il y aurait lieu aussi de demander que les mélanges auxquels nous faisons allusion (matières destinées à la fabrication des explosifs, mais pratiquement insensibles au choc et peu inflammables) soient considérés comme marchandises ordinaires et puissent voyager comme telles, sans entrave d'aucune sorte.

Agréez, etc.

V.—NOTE DE M. LUNDHOLM

Londres, le 26 avril 1912.

J'ai examiné les observations formulées dans divers pays et portées à la connaissance de la Commission par votre lettre-circulaire du 12 mars 1912. Je ne crois pas que notre but puisse être atteint par le choix d'un petit nombre d'épreuves seulement, parce que les dangers des explosifs, déjà nombreux, augmentent au fur et à mesure de l'apparition de nouveaux groupes.

Le désir de n'avoir que quelques épreuves simples est commun; mais, comme ces épreuves doivent constituer une garantie que les explosifs qui les ont subies sont propres au transport, à l'emploi et à un emmagasinage prolongé dans des climats variés, sans danger, un petit nombre d'épreuves ne suffisent pas, à mon avis.

Un certificat de composition donné par un fabricant étranger et intéressé, ne pourrait pas non plus être considéré comme suffisant. Le risque pour le public est trop grand.

Voici quelques exemples pour montrer de quelle façon les épreuves ont augmenté en Grande-Bretagne.

Lorsque le fulmi-coton était le seul explosif brisant,—car la nitroglycérine était interdite,—l'épreuve d'Abel, la détermination de la température de détonation et l'examen au papier tournesol étaient les seules épreuves en vogue.

Lorsque la dynamite à la Guhr fut inventée, l'épreuve d'Abel resta comme épreuve de stabilité chimique, quoiqu'on y apportât quelques changements en pratique. Mais, en outre, il fallait inventer des épreuves d'exsudation et de sensibilité à la friction et au choc. Lors de l'introduction des explosifs gommes, on a gardé l'épreuve d'Abel pour la stabilité chimique, mais il fallut en modifier le mode d'emploi; on conserva les autres épreuves et on en ajouta une pour la liquéfaction.

Avec l'introduction du chlorate de potasse dans les explosifs, ou dut instaurer une épreuve pour la sensibilité plus grande à la friction causée par un long emmagasinage, pour la facilité d'ignition et pour la combustion spontanée. Les nitrates de soude et d'ammoniaque ont soulevé la question d'absorption de l'humidité, et la présence d'humidité suggéra la possibilité d'une réaction entre les ingrédients d'un explosif en magasin.

En Allemagne, où on peut transporter certains explosifs par chemin de fer comme marchandises, en quantités limitées ou illimitées, il devint nécessaire d'avoir d'autres épreuves encore.

Pour illustrer la difficulté et la façon de la tourner, supposons qu'un explosif *Ex . . . ite* ait été inventé en Belgique; on ne considérerait pas comme sûre l'importation de cet explosif en Grande-Bretagne, sur la simple preuve de ce qu'il donne des résultats satisfaisants lorsqu'on le soumet: 1° à un essai au mouton; 2° à un essai de résistance au feu, et 3° à la chaleur, même si, outre cela, on a pu obtenir des fabricants un certificat de sa composition et des épreuves qu'il a subies à l'usine.

Mais s'il ne faut pas s'attendre à ce qu'*Ex . . . ite* soit introduit en Grande-Bretagne, sur la simple foi de quelques épreuves ordinaires, il pourrait facilement être importé s'il avait été d'abord expérimenté par le Ministère de l'Intérieur de Grande-Bretagne et placé sur la "liste autorisée." Un douanier prend des échantillons d'un explosif autorisé, à son arrivée, et permission est donnée de transporter et emmagasiner l'explosif jusqu'à ce que les épreuves soient terminées, ce qui prend au plus dix jours, après quoi, si l'épreuve est satisfaisante, l'explosif est admis à la consommation immédiate.

L'unification des épreuves serait alors très simplifiée, parce qu'il n'y aurait pas besoin de l'appliquer aux épreuves d'autorisation. Chaque pays se servirait de ses épreuves pour placer un explosif sur sa "liste autorisée." L'uniformité ne s'appliquerait alors qu'aux épreuves ordinaires lors de l'importation d'un explosif autorisé.

L'épreuve de stabilité chimique pour la Grande-Bretagne sera et restera l'épreuve d'Abel. Un comité d'experts fut formé il y a trois ans par le Gouvernement, sous la présidence du Commandant Cooper-Key, Inspecteur en chef des explosifs de S. M. —Les Ministères de l'Intérieur, de la Guerre et de la Marine et de l'Industrie sont représentés dans ce comité, et un certain nombre d'importants laboratoires ont contribué à ses investigations. A la première séance du comité, il fut décidé, à l'unanimité, qu'aucune épreuve, dans aucun pays connu des membres, ne pourrait remplacer l'épreuve d'Abel pour les épreuves de stabilité des classes d'explosifs pour lesquelles on l'emploie dejà, mais que cette épreuve a des défauts auxquels il faudrait remédier. Le Comité a essayé depuis trois ans d'établir un type d'appareils, de produits chimiques et de méthodes de se servir de l'épreuve pour divers explosifs, mais il y a encore à faire avant que toutes les causes de différences soient éliminées. Il résulte de celà, cependant, que l'épreuve d'Abel restera plus que jamais l'épreuve de stabilité des classes d'explosifs à la nitroglycérine et à la nitrocellulose, pour la Grande-Bretagne, ses colonies et protectorats.

Vu les raisons exposées ci-dessus, je proposerai:

1° Que chaque pays fasse essayer les explosifs présentés à l'examen, de la manière que des experts considéreraient comme nécessaire, de manière à prouver que ces explosifs sont propres au transport, à l'emploi et à l'emmagasinage, pour de longues périodes, dans les conditions climatériques de ces pays et celles de leurs colonies; que les explosifs qui résistent à l'épreuve, et seulement ceux-ci, soient placés sur la liste comme "autorisés."

2° Que les explosifs autorisés importés soient fabriqués à l'usine d'où viennent les échantillons, et exactement de la même manière que les échantillons qui ont subi avec succès l'épreuve pour l'autorisation.

3° Qu'un explosif sur la liste "autorisée" puisse être importé grâce à une licence délivrée par l'autorité compétente. La demande de licence devrait donner la composition de l'explosif et déclarer que c'est la même, chimiquement et physiquement, que celle de même dénomination figurant sur la liste "autorisée." A l'arrivée du chargement, les officiers de douane, ou toute autre personne autorisée, prennent un échantillon et le remettent au laboratoire des chimistes du Gouvernement. L'officier de douane, ou toute autre personne autorisée, devra aussi s'assurer que l'emballage est fait suivant les règles.

4° L'explosif devra être transporté dans un magasin pour y être emmagasiné, mais ne doit pas être enlevé de là jusqu'à autorisation de l'autorité compétente.

Les épreuves seront les suivantes:

1° Analyse pour vérifier la composition;

2° Epreuve d'Abel pour la stabilité chimique, pour les explosifs contenant de la nitroglycérine ou des nitrocelluloses;

3° Examen visuel pour l'exsudation et la consistance, pour les explosifs contenant de la nitroglycérine.

L'autorité compétente pourrait avoir le droit d'autoriser l'importation des explosifs non autorisés pour des buts spéciaux dans des conditions qui donneraient une protection raisonnable au public.

Agréez, etc.

M. le Colonel Vitali a déclaré préférer exposer ses vues à la réunion de Paris.

M. Spica fait a savoir qu'il acceptait les propositions faites, d'autant plus que l'on pourra encore débattre les points de détail.

Comme vous l'aurez vu par les notes reproduites ci-dessus, l'accord n'est pas loin d'être fait en principe sur les propositions que nous avons eu l'honneur de vous soumettre; à part la manière de voir de M. Lundholm, d'après laquelle, semble-t-il, les travaux de notre Commission ne pourraient aboutir, les observations présentées visent plutôt des points de détails qui pourront être rapidement réglés le 24 juin; nos propositions n'étaient naturellement qu'une ébauche et les remarques de divers de nos collègues sont parfaitement fondées: les détonateurs doivent former une classe spéciale; certaines compositions dangereuses doivent être exclues à priori; il faut déterminer les conditions exactes de l'épreuve du mouton et au fer rouge, etc.

Il appartiendra à la Commission de préciser tous ces points dans la réunion du 24 juin.

Comme ce sera vraisemblablement l'unique réunion préalable et que plusieurs d'entre-nous, sans doute, ne pourront assister au Congrès, nous vous prions de vouloir bien, d'ici au 24 juin, examiner attentivement les notes ci-jointes et préparer des conclusions que nous puissions adopter définitivement, de façon à ce qu'un rapport final puisse être établi sur ces bases.

Dans le cas ou vous seriez empêché de vous rendre à la réunion du 24 juin, nous vous serions bien obligés de nous faire parvenir plusieurs jours avant cette date, l'exposé de votre manière de voir et vos propositions.

Agréez, Monsieur et Cher Collègue, l'assurance de notre considération la plus distinguée.

Le Secrétaire, *Le Président,*
AD. BREYRE. V. WATTEYNE.

ANNEXE III

Lettre de M. Gey van Pittius

Malabar (près Bandoeng), le 27 avril 1912.

En réponse à votre lettre du 12 mars, j'ai l'honneur de vous communiquer que je suis entièrement d'accord avec vous sur la classification des explosifs d'après leurs qualités et non d'après leur composition chimique. Seulement je me permets de soumettre à votre haute compétence les observations suivantes:

Dans la composition des poudres sans fumée, il faut lire: Nitrocellulose *plus ou moins* gélatinisée, 0 à 10%, puisqu'il y a des poudres de chasse contenant des salpêtres, qui ne sont pas tout à fait gélatinisées, en outre il y a poudres à tir blanc (pour usage militaire) qui ne sont pas gélatinisées du tout.

De même, il faut lire à la dernière ligne: nitrate de baryum, de potassium, *amidon*, etc., vu qu'il y a des poudres peu gélatinisées qui contiennent de l'amidon.

Dans la composition des explosifs de la classe III, il faut ajouter: Nitrocellulose, 0 à 1%, puisque parmi les explosifs de sûreté, il y en a qui contiennent de la nitroglycérine qui généralement est gélatinisée (avec la nitrocellulose).

Au perchlorate d'ammonium, il faut ajouter les perchlorates de potasse et de sodium.

Dans l'essai de résistance à la chaleur, il faut ajouter après "perte de poids," *en plus de la perte d'eau hygroscopique.*

En ce qui regarde l'essai de résistance au feu, je crains que cette épreuve au "fer rouge" (outre la question de degré, rouge foncé, rouge clair, blanc rougeâtre) ne soit trop rigoureuse pour les *cheddites* qui en général sont considérées comme explosifs de sûreté (p. e. en Algérie) et qui, une fois allumées, ne s'éteignent pas en retirant la source de chaleur. Il m'est pourtant impossible de présenter en considération une autre épreuve que l'épreuve, rude et peu scientifique, qui consiste à brûler, sur un bûcher, de grandes quantités (25 à 200 kilogrammes) d'explosifs, dans des caisses doublées de zinc ou de fer blanc.

Quant à la question qu'émet le professeur Heise, je crois que tous les explosifs nécessitent plus ou moins le contrôle auquel M. Heise veut soumettre la poudre à nitrocellulose, puisque les explosifs à base de chlorate et de perchlorate deviennent dangereux s'ils contiennent des acides, ou si à cause d'impuretés le chlorate d'ammonium peut se former par des réactions intérieures.

Or je suis d'avis que, pour prévenir ces dangers, toutes les fabriques d'explosifs doivent être surveillées par des inspecteurs gouvernementaux, non seulement pour prévenir le danger de la fabrication, mais surtout pour l'emmagasinage quand il s'agit d'explosifs fraîchement confectionnés. Cette question d'emmagasinage nous ferait entrer pour le moment trop dans les organisations des différents gouvernements et je crois que nous ferions mieux de la séparer du transport et de nous occuper surtout de ce dernier. Pratiquement, la fabrication des explosifs est suffisamment surveillée pour que le transport d'explosifs fraîchement préparés, classifiés et admis au transport, n'offre aucun danger. Outre les documents, prouvant la nature et la classification, il suffira d'ajouter la preuve que l'explosif est de fabrication récente (p. e. moins de trois mois). Dans le cas contraire, il serait nécessaire d'exiger encore un document prouvant qu'un examen spécial par un chimiste compétent a eu lieu, document qui devrait être légalisé par le consulat du pays dans lequel le transport entrera.

Voyez à cet égard les prescriptions des Indes Néerlandaises (*Staatsblad van Nederlandsch-Indie,* n°. 234, pp. 5 et 6) contenant la prescription suivante: "Les explosifs qui ont été emmagasinés plus longtemps que trois mois et que l'on veut transporter doivent être soumis à l'examen d'une Commission nommée par le chef de la province ou de la commune intéressée."

Agréez, etc.

ANNEXE IV

2me Note de M. Lundholm

Londres 10 juin 1912.

J'ai le plaisir de vous accuser réception des dernières communications des Membres de la Commission contenues dans votre circulaire du 18 mai.

Le but de la Commission est l'unification des épreuves d'explosifs, et si on pouvait en réduire le nombre, cela faciliterait beaucoup notre tâche. Mais, si l'on prend en considération l'origine et le développement des épreuves, on verra qu'au commencement il y en avait peu, et que les deux facteurs auxquels est dû leur accroissement sont: la découverte graduelle de défauts dangereux dans les explosifs, et l'introduction de nouvelles classes d'explosifs pour lesquels les anciennes épreuves ne suffisaient pas. Si on considère que le but des épreuves est de protéger le public, c'est-à-dire de garantir que la fabrication, le transport, l'emmagasinage et l'emploi des explosifs offrent le moins de danger possible, non seulement dans les conditions climatériques du pays de fabrication, mais aussi dans tous les pays où ils pourraient être exportés, il semble qu'on ne puisse réduire le nombre d'épreuves qu'en unifiant celles qui ont été différemment élaborées dans divers pays, mais dans le même but.

Si donc on ne peut réduire matériellement le nombre des épreuves, il est impossible de les unifier à temps pour le prochain Congrès, surtout s'il est nécessaire de faire des recherches sérieuses et s'il faut faire différentes épreuves comparatives dans le même but, afin de pouvoir faire un choix des meilleures pour le concours.

Vous suggérez, Monsieur le Président, que si on tombe d'accord sur quelques-unes des épreuves, d'autres suivront. Je suis tout-à-fait d'accord avec vous sur ce point. Cela voudrait dire que la continuation du Comité est nécessaire, parce que si on ne se met d'accord maintenant que sur quelques épreuves, cela n'amènerait pas le but ultérieur de l'unification des épreuves, qui, à mon avis, signifie l'établissement de conditions techniques d'après lesquelles, dans l'opinion de la Commission les explosifs pourraient, sans danger pour le public, être transportés, emmagasinés et employés dans tous les pays du monde, sans tenir compte du lieu d'origine.

Mes propositions du 26 avril émanent des obstacles que j'ai vus à la réduction matérielle du nombre des épreuves d'explosifs des qualités existant maintenant,

La proposition faite d'établir une série "nationale"[1] d'épreuves pour l'autorisation d'un explosif, et ensuite une épreuve peu sévère de "consignation" donnerait des résultats immédiats et ne s'opposerait en aucune manière à l'unification des épreuves.

Si on s'entendait pour accepter le principe de deux séries d'épreuves, chaque nation qui préférerait des épreuves indépendantes pourrait préparer une liste d'explosifs autorisables, d'après des échantillons soumis de l'étranger. Les épreuves allemandes doivent être plus strictes que les anglaises sous certains rapports parce que l'Allemagne a trois classes pour le transport par chemin de fer: une pour les dynamites, etc., et deux pour les explosifs moins dangereux qui sont transportés comme marchandises ordinaires, tandis que la Grande-Bretagne n'a qu'une classe, tous les explosifs devant être transportés comme dynamite. D'autre part, les épreuves de stabilisation, combustion spontanée, etc., doivent être plus sévères en Grande-Bretagne à cause de la grande quantité, principalement d'explosifs à base de nitroglycérine, qui sont exportés dans des climats chauds, et qui doivent être à même de supporter les conditions existant dans les pays où ils sont expédiés.

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[1] Propre à chaque pays.

L'épreuve d'autorisation prendrait du temps, mais une fois un explosif autorisé, l'épreuve de consignation ne devrait donner aucune peine. L'expérience longue et variée du Ministère de l'Intérieur anglais a prouvé qu'il était suffisant de faire une analyse d'identification et d'employer en outre l'épreuve de chaleur d'Abel pour les explosifs contenant de la nitroglycérine et de la nitrocellulose.

Pour les analyses, les chimistes du Gouvernement demandent dix jours, et, de fait, l'explosif importé devrait être emmagasiné jusqu'à ce qu'il soit libéré par un ordre du Ministère de l'Interiéur. Pour les maisons connues on n'insiste pas sur l'emmagasinage, quoique la maison soit considérée comme responsable si l'analyse subséquente prouve que l'explosif importé n'est pas identique à celui qui est autorisé.

Si la Commission n'admet pas qu'un explosif qui a passé un petit nombre d'épreuves soit déclaré suffisamment sûr pour qu'il puisse être fabriqué, transporté, emmagasiné et employé dans tout climat où on se sert d'explosifs, et s'il est difficile à la prochaine assemblée de tomber d'accord sur des épreuves uniformes en nombre suffisant, les propositions que j'ai faites dans ma lettre du 26 avril semblent s'approcher du but final de l'unification des épreuves, c'est-à-dire l'admission des explosifs de tous les autres pays, et elles ne viendront pas à l'encontre des efforts continus faits pour arriver tôt ou tard à une complète unification des épreuves, si la Commission est renommée par le Congrès de Washington-New-York.

Agréez, etc.

ANNEXE V

2^me^ Note de M. Jacqué

La Cantabrica, 22 juin 1912.

NOTE RELATIVE AUX MÉTHODES D'ÉPREUVES DES EXPLOSIFS

S'il est peut-être impossible de faire admettre par tous les pays une règlementation uniforme dans tous ses termes, il paraît au contraire assez facile de se mettre d'accord: 1° sur les types qui devront servir en tous lieux de points de comparaison; 2° sur les méthodes d'épreuves à adopter partout d'une façon définitive.

Je crois donc que ce sont là les deux points qu'il y a lieu de discuter avant tout.

I.—DES TYPES À ADOPTER

Ces types devront être assez simples pour qu'on puisse toujours les élaborer n'importe où. Il semble qu'ils peuvent être réduits à cinq ou six qui seraient:

1° Les détonateurs.—Aucun doute ne subsiste sur ce genre de produits, qui, employés en petite quantité, sont susceptibles de faire détoner des masses plus ou moins considérables d'explosifs moins sensibles qu'eux. Le fulminate de mercure, qui est tout indiqué, sans être extraordinairement sensible, l'est assez pour servir de type à ce genre de produits.

2° Dynamites et explosifs à haut taux de chlorate ou perchlorate:

La dynamite n° 1 à 75% et un explosif chloraté ou perchloraté, contenant 12% de paraffine pour 88% de sels de potasse finement moulus, pourraient être adoptés.

3° Classes des explosifs moins sensibles au choc (à faible titre de nitroglycérine ou à taux moyen de chlorates ou perchlorates.

On pourrait adopter comme types de ce groupe:

a) Un mélange intime de 9 nitroglycérine, 9 farine torréfiée et 82 nitrate d'ammoniaque;

b) 35 perchlorate de potasse, 46 nitrate d'ammoniaque, 12 trinitoluène, 7 amidon torréfié.

4° Le quatrième groupe serait formé par les explosifs dont les propriétés de sensibilité au choc et à l'inflammation ne dépasseraient pas celles d'un type Favier qui pourraît être par exemple: 92 nitrate d'ammoniaque, 5 trinitoluène, 3 tétranitronaphtaline.

Ces explosifs pourraient contenir une quantité de perchlorates ne dépassant pas 30 à 40% à la condition d'être comparables en tout au précédent type et pourvu qu'il n'y ait pas incompatabilité entre les substances employées.

5° Le cinquième groupe serait constitué par les explosifs incomplets (hydrocarbures liquides pouvant contenir jusqu'à 10% de nitroglycérines difficilement congélables, mais avec une quantité d'oxygène beaucoup trop faible pour que les combustions réalisées partiellement puissent d'elles-mêmes se propager dans la masse.

6° Dans le sixième groupe entreraient les différentes sortes de poudres de chasse ou de guerre.

Les types pourraient être une poudre noire ordinaire et la balistite à 50/50 normalement stabilisée.

II.—EPREUVES

Laissant de côté les épreuves spéciales aux poudres sans fumée et aux nitrocelluloses pour lesquelles on n'aura pas de mal à se mettre d'accord, il y a lieu de fixer les idées sur l'épreuve de chaleur, l'épreuve du mouton et enfin les épreuves d'inflammabilité et de susceptibilité de détonation par incendie.

a) *Epreuve de chaleur*

Toute étuve munie d'un thermostat peut servir à cette épreuve. On pourrait exiger qu'après le chauffage dont la durée à discuter, l'acidité totale de la matière dosée volumétriquement n'ait pas varié sensiblement et que les autres épreuves appliquées avant et après la dessication donnent des résultats tellement comparables entre eux, que seule la perte d'eau hygroscopique puisse justifier les différences si elles existent.

Il y aurait bien entendu â examiner l'exsudation dans le cas des explosifs à la nitroglycérine.

b) *Essais au choc*

D'après les différentes notes, il semble que la méthode anglaise de la chute d'une sphère maintenue par un électro-aimant, dont le courant peut être interrompu à volonté a réuni la plupart des suffrages. Encore faudrait-il s'entendre sur les dispositions de détail qui permettront d'avoir des résultats absolument comparables (mode de fixation de l'explosif sur le grain du socle, poids d'explosif à employer, etc.)

On pourrait, bien entendu, répéter les essais en mélangeant l'explosif avec une certaine quantité de verre pilé, afin d'avoir un idée de sa sensibilité à la friction.

c) *Epreuves d'inflammabilité*

Ces épreuves pourraient comporter trois essais: 1° essai au fer rouge, 2° chauffage progressif dans une capsule en porcelaine, 3° essai d'inflammation au bec de Bunsen.

1° Pour l'essai au fer rouge, il convient d'opérer à une température aussi comparable que possible dans tous les cas. Le mieux est d'introduire le fer, qui peut être par exemple une baguette de 10 millimètres de diamètre, terminée en pointe dans une grille électrique d'Heræus; on fixe la température en observant le moment où fond l'aluminium par exemple, ou encore un alliage de fer et d'aluminium. Si l'on veut encore plus d'exactitude, il suffit d'employer deux petites nacelles renfermant deux alliages de points de fusion voisins, mais cependant assez distincts pour que le premier alliage soit franchement fondu quand l'autre est encore solide. On retire alors la baguette qui porte un manche en bois à l'extrémité qui sort de l'appareil et on l'introduit immédiatement dans la cartouche après s'être assuré préalablement que la nature de l'explosif permet de faire cette expérience sans danger.

Il y a lieu de fixer la longueur de la partie de la baguette qui pénètre dans la grille.

2° Le chauffage progressif dans une petite capsule ne présente pas de difficultés; il est facile de le règlementer en fixant simplement la quantité d'explosif qui doit être soumise à l'essai (20 grammes par exemple) et le nombre de degrés dont devra s'élever la température dans l'unité de temps.

3° Quant à l'inflammation au bec de Bunsen, il convient seulement de dire sur quel support on doit placer la matière à essayer; à mon avis, le meilleur est le carton d'amiante.

Tels sont les points qu'il faut avant tout élucider. Cela fait, il serait facile, dans l'espace d'un mois, d'examiner les résultats que nous aurons obtenus dans les mêmes conditions, avec les mêmes appareils, et de vérifier s'ils sont bien comparables et s'il ne peut surgir de ce fait aucune contestation ni aucune indétermination dans le classement que nous proposons de faire.

ANNEXE VI

COMMISSION INTERNATIONALE POUR L'ÉTUDE DE L'UNIFICATION DES MÉTHODES D'ÉPREUVE SUR LA STABILITÉ DES EXPLOSIFS

Procès-Verbal des réunions du 24 juin 1912, à Paris

Sont présents:

MM. Watteyne, président;
Barthélemy, Vitali, Will, Jacqué, membres de la Comsion;
Mente, collaborateur de M. Will;
Beyling, délégué par M. Heise, empêché;
Ad. Breyre, secrétaire de la Commission.

M. Schmerber, Ingénieur, assiste à la séance comme interprête, pour faciliter la discussion.

En ouvrant la séance à 10 heures, M. le Président rend un hommage ému à la mémoire de M. l'Ingénieur en chef Stassart, secrétaire de la Commission, enlevé inopinément, au début de 1911, à ses travaux et à l'amitié de tous ceux qui l'ont connu.

MM. Barthélemy, Jacqué, Vitali et Will, au nom de tous les collègues, s'associent à ces paroles.

M. le Président remercie spécialement notre collègue M. Barthélemy qui, non content de recevoir si gracieusement la commission, s'est encore chargé d'organiser une visite très intéressante à la station d'essais de Liévin.

M. le Président donne lecture des lettres d'excuse de MM. Bichel, Lundholm, Gey van Pittius et Spica, empêchés de se trouver à la réunion.

Il est donné lecture des notes de MM. Gey van Pittius et Lundholm, reçues postérieurement à l'envoi de la circulaire du 18 mai 1912 (annexes III et IV).

M. Gey van Pittius présente quelques observations de détail relativement à la classification proposée par la circulaire du 12 mars 1912.

M. Lundholm maintient la manière de voir exposée dans une lettre antérieure, mais en précisant sa pensée qui serait de laisser à chaque pays le soin d'établir, comme il l'entend, les essais de reconnaissance d'un explosif, tout en tâchant d'unifier les essais sommaires de "consignation" à l'entrée d'un pays.

M. Jacqué a également remis une note tendant à fixer les détails des épreuves proposées et qui figure aux annexes (annexe V).

M. le Président fait l'exposé de la situation et résume les travaux accomplis et les idées échangées. Il signale notamment la remarquable réglementation allemande, à laquelle plusieurs de nos collègues ont personnellement collaboré. Cette règlementation parait, malgré quelques critiques, donner d'excellents résultats en Allemagne, mais elle est trop étendue pour être d'application internationale. Il pense que, si l'on veut aboutir, la Commission doit s'attacher à fixer quelques points précis et déterminer quelques épreuves susceptibles d'une application internationale. C'est le moyen d'arriver sinon à une solution complète, du moins à une solution pratique, qui constituera déjà un progrès sérieux.

Il est entendu que les détonateurs doivent former une classe spéciale, puisque leur transport ne peut s'effecteur que dans des conditions d'emballage toutes spéciales et en l'absence d'autres explosifs; la Commission ne s'en occupera pas, non plus que des explosifs de tir et de chasse qui ne sont pas des explosifs industriels.

M. Will expose comment, en Allemagne, alors qu'on était parti avec l'idée de simplifier le plus possible, on est arrivé, par la force des choses, à l'ensemble quelque peu compliqué du règlement actuel allemand. Ainsi la question de l'emballage a une importance capitale: un emballage spécial peut équilibrer le danger inhérent à l'explosif â transporter. C'est à cause des difficultés pratiques que l'on est venu à créer une série d'explosifs-types, à propriétés bien caractérisées, à essayer chaque fois en même temps que l'explosif à expérimenter.

Un autre principe est de laisser aux fabricants, sous leur responsabilité, le soin de contrôler leurs produits dans leurs laboratoires. On n'a pas encore eu à regretter cette confiance qu'on a accordée aux industriels.

M. Vitali signale le prochain Congrès international des Transports qui va se tenir à Berne, où la Commission internationale des transports des explosifs n'aura à s'occuper que de trois explosifs bien connus (en dehors des munitions de sûreté): acide picrique, trinitrotoluène, nitrocellulose humide. Il sera utile de communiquer nos conclusions à cet organisme.

M. le Président propose de passer immédiatement à l'élaboration des conclusions en prenant pour point de départ l'avant-projet contenu dans la lettre du 12 mars 1912.

M. Barthélemy demande que la Commission, dans ses conclusions, attire l'attention sur le rôle important de l'emballage, qui, bien conçu, permet de transporter les explosifs par grande vitesse en toute sécurité.

Conformément aux propositions émises dans la note du 12 mars 1912, M. le Président propose de définir d'abord une .épreuve d'élimination, applicable à tous les explosifs industriels, suivie d'une série d'autres permettant de les classer dans des catégories bien distinctes au point de vue des dangers qui leur sont propres.

La première épreuve, dont le texte va être donné, devait ainsi s'appeler "éprevue d'*elimination.*" Mais, au cours de la discussion, MM. Will et Mente ont fait remarquer que, par ces mots, on entrerait trop dans l'*application*, qu'il convient de réserver à l'appréciation des divers gouvernements, ceux-ci pouvant juger que le transport d'explosifs sensibles serait quand même admissible sous certaines conditions de quantités réduites et d'emballage spécialement soigné. La Commission doit se borner indiquer des épreuves.

Pour tenir compte de cette observation, l'expression *épréuve d'élimination* a été remplacée par les mots *épreuve préalable.*

Après quelques observations encore, la Commission se rallie unanimement à la définition suivante:

I.—EPREUVE PRÉALABLE

Deux échantillons, chacun de 10 grammes d'explosif non desséché, sont disposes dans des capsules de verre, munies d'un couvercle simplement posé, de 35 millimètres de diamètre et de 50 millimètres de hauteur; ils sont introduits dans une étuve chauffée à 75° où ils séjournent pendant quarante-huit heures. Où s'assure qu'il n'y a aucune décomposition de l'explosif, ni aucune modification notable *dans l'aspect ou dans l'odeur. Pour les explosifs nitrés, il ne doit y avoir aucun dégagement de vapeurs rutilantes.*[1]

La séance est levée à 12 h. 45 et reprise à 15 heures.

La Commission aborde la question d'une épreuve au choc.

Il faut ici une matière de comparaison, tout au moins pour limiter les explosifs peu sensibles au choc.

Après échange de vues, M. Will propose d'employer à cet effet de *l'acide picrique* pur pulvérisé, matière facile à se procurer et constamment semblable à elle-même.

M. Vitali appuie la proposition et la Commission se rallie à cet avis.

A titre de renseignement M. Will indique qu'avec un mouton de 2 kilogrammes, l'acide picrique détone sur une hauteur moyenne de 65–68 centimètres avec un écart maximum de ± 8 centimètres.

M. Beyling voudrait voir préconiser la chute libre du mouton, sans guidage, et le lâcher électrique, comme dans la méthode anglaise.

M. Will pense qu'il est tout à fait inutile de préciser le type du mouton, son poids, etc., pourvu que les essais se fassent chaque fois le même jour, avec le même appareil, dans des conditions identiques pour l'acide picrique et l'explosif à comparer.

La Commission se rallie à cette manière de voir, en renvoyant, pour le surplus, aux rapports antérieurs contenant la description des appareils que l'on peut employer.

L'épreuve n°. II est définie comme suit:

II.—EPREUVE DE RÉSISTANCE AU CHOC

On essaiera des poids égaux de l'explosif à expérimenter, préalablement pulvérisé et desséché, d'une part, et d'acide picrique pur pulvérisé et sec, d'autre part, avec le même appareil et dans des

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[1] M. Lundholm, empêché d'assister à la séance de Paris, a demandé, par lettre du 23 juillet 1912, d'ajouter à ce texte la réserve suivante:

"N. B.—Bien qu'aucun explosif ne soit considéré comme suffisamment stable s'il n'a pas passé cette épreuve, il ne s'ensuit par qu'un explosif qui la passe soit nécessairement suffisamment sûr pour être inclus parmi les explosifs pratiques."

Il ne nous a plus été possible de consulter les collègues à ce suject. Nous donnons acte de cette réserve à M. Lundholm. (NOTE DU BUREAU.)

conditions identiques. Les prises d'essai, de 5 à 10 centigrammes chacune, seront disposées sur une enclume en acier en une couche occupant 1^{cm}27 de diamètre. L'explosif est recouvert d'un cylindre en acier trempé de 1^{cm} 27 de diamètre et de même hauteur. Dix essais consécutifs seront exécutés avec chacun des explosifs et serviront à determiner la hauteur de chute moyenne qui provoque l'explosion.

Les explosifs considérés comme peu sensibles au choc doivent montrer une insensibilité au moins égale à celle de l'acide picrique pur pulvérisé.

N. B.—Peuvent être notamment employés pour cet essai, soit l'appareil anglais à chute libre, soit les appareils décrits au VI^{e} Congrès international de Chimie appliquée (Rome 1906).

M. Will fait remarquer que l'essai qui vient d'être défini ne renseigne pas sur la résistance à la friction, qui est importante, spécialement pour certains explosifs au chlorate, dont les essais au choc simple pourraient donner une fausse idée de leur sécurité.

M. Jacqué préconise de faire des essais au choc en mélangeant à l'explosif un pourcentage de verre pilé: l'explosif, en s'échappant sous le choc du mouton, subit une friction sur le verre pilé.

M. le Président suggère d'opérer une partie des dix essais prescrits ci-dessus, avec verre pilé.

M. Vitali demande si l'on connait les résultats que donnerait l'acide picrique dans ces conditions; comme il n'y a pas d'expériences suffisantes à ce sujet, il vaut mieux ne pas prescrire ce genre d'épreuve.

M. Will dit qu'il opère toujours dans un mortier à parois rugueuses (en biscuit), par comparaison avec une quantité égale d'acide picrique. Cette expérience, quoique d'apparence peu scientifique, est très suffisante quand on opère par comparaison: il n'est même pas nécessaire de préciser les détails de l'essai, du moment qu'on exige qu'il se fasse dans les conditions identiques pour les deux corps à comparer.

L'essai à la friction est admis, et défini comme suit:

II *bis*.—EPREUVE DE RÉSISTANCE A LA FRICTION

L'explosif placé dans un mortier en biscuit légèrement chauffé (20 à 30° centigrades), ne doit pas se montrer moins résistant à la *friction que l'acide picrique pur pulvérisé soumis, dans le même appareil, à une expérience identique.*

La Commission étudie ensuite un essai de résistance au feu.

L'essai à la mèche est adopté sans discussion dans les termes du règlement allemand.

Un long échange de vues se produit sur les épreuves à haute température, et sur le point de savoir s'il faut indiquer un explosif-type pour agir par comparaison.

M. Mente croit qu'il n'est pas nécessaire d'indiquer cet explosif-type, les conditions de cet essai pouvant se écrire aisément.

La Commission se rallie finalement à cet avis: après discussion, les textes suivants sont adoptés:

a) EPREUVE A LA MÈCHE: *3 grammes d'explosif pulvérulent sont versés dans un tube-éprouvette en verre: par de légers chocs, on donne à la substance une surface bien unie. On y introduit alors une mèche de poudre brûlant lentement (1 centimètre par seconde). L'essai est répété deux fois.* L'inflammation caractérise les poudres déflagrantes et les explosifs facilement inflammables.

b) EPREUVE SUR UNE CAPSULE DE FER PORTÉE AU ROUGE: Les explosifs ayant supporté l'essai précédent sans déflagration seront soumis à un essai à haute température pour s'assurer de leur inaptitude à la détonation sous l'action du feu.

Une capsule en fer, hémisphérique, de 12 centimètres de diamètre, 1 millimètre d'épaisseur, est portée au rouge sur un brûleur: on y verse d'abord une petite quantité (0.5 gr.) de la substance pulvérisée, puis, s'il ne survient pas de détonation, on augmente la quantité jusque 5 gram. L'épreuve est recommencée deux fois.[1]

c) L'EPREUVE AU FER ROUGE a pour but de constater l'inaptitude des explosifs de sûreté à l'inflammation.

Après quelques essais préliminatires sur de petites quantités pour constater d'abord le peu d'inflammabilité relative du produit, on dispose 100 grammes d'explosif sur un carton d'amiante; on met en contact avec l'explosif l'extrémité d'une barre de fer de 15 millimètres de diamètre, portée au rouge cerise (900° environ) sur 10 centimètres de longueur. La matière peut brûler lentement, sans

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[1] Sur une observation ultérieure de M. Barthélemy, les conclusions portent: *L'essai est repété* TROIS *fois.*

donner lieu à aucune explosion, et doit s'éteindre lorsqu'on retire la source de chaleur.

M. Breyre fait remarquer qu'on a abandonné la notion des explosifs-types permettant de délimiter les classes par comparaison; on n'a conservé le principe que pour l'épreuve au choc et à la friction.

Ne faudrait-il pas proposer une classification résultant des essais préconisés?

M. Mente pense qu'il est prématuré d'aller plus avant dans l'œuvre d'unification, les classifications dépendant aussi des règles de transport spéciales à chaque pays.

M. le Président pense que, sans imposer une classification, le rapport final de la Commission peut la suggérer en déduction des épreuves admises. Au surplus, la sanction de nos travaux serait la réunion, par les divers Gouvernements intéressés, d'une convention munie de pouvoirs officiels et qui pourra, sur la base du rapport final de notre Commission, provoquer l'unification des épreuves et l'unification des classification dans les transports internationaux.

M. le Président clôture les travaux en remerciant les membres présents d'avoir bien voulu se déranger de si loin pour assister à ces séances; il remercie chacun du concours dévoué apporté à l'élucidation d'un problème aussi ardu et émet l'avis que les conclusions de la Commission consacreront un progrès réel sur l'état de choses actuel.

La séance est levée à 19 h. 15.

Le Secrétaire,
AD. BREYRE.

Le Président,
V. WATTEYNE.

INTERNATIONAL COMMISSION FOR UNIFICATION OF THE TESTING METHODS ON THE STABILITY OF THE EXPLOSIVES

Final Report (July 25, 1912) to be Presented to the Eighth International Congress of Applied Chemistry

I. A Brief Account of the Work of the Commission

Before formulating our conclusions in this report which follows the report presented at the London Congress of 1909 and published among the publications of the Seventh Congress (Section III b—Explosives—pages 130 to 190), we beg to remind the Commissions work from its beginning and how it came to the present conclusions which we beg to submit for ratification to the Seventh Congress of Applied Chemistry at New York, 1912.

The Commission was established at Rome in 1906, at the Sixth Congress of Applied Chemistry. Section III b (explosives) of the said Congress having recognized the opportunity of uniforming the testing methods with regard to the stability of explosives, elected an international Commission[1] with a view of studying the question and of submitting to the following Congress such conclusions as could be used as a basis for the projected unification.

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[1] Ont été désignés pour faire partie de cette Commission:

Pour l'*Allemagne:* MM. Professeur W. Will, à Berlin; Professeur H.-F. Lenze, à Charlottenburg; Professeur F. Heise, à Bochum; Directeur général C.-E. Bichel, à Hambourg;

Pour l'*Espagne:* M. M. Jacque, à Bilbao;

Pour la *France:* M. L. Barthelemy, à Paris;

Pour la *Grande-Bretagne:* MM. C.-O. Lundholm, à Stevenson, et Professeur W. F. Reid, à Addlestone;

Pour l'*Italie:* MM. Colonel G. Vitali, à Rome, et Professeur G. Spira, à Venise;

Pour les *Pays-Bas:* M. le Capitaine Gey van Pittius, à Amsterdam;

Pour la *Russie:* M. Professeur Saphojnikoff, à Saint-Petersbourg;

Pour la *Belgique:* MM. Inspecteur général des mines V. Watteyne, à Bruxelles, et Ingénieur en chef Directeur des mines S. Stassart, à Mons.

MM. Watteyne et Stassart, ont été nommés respectivement Président et Secrétaire de la Commission.

M. Stassart étant décédé le 21 janvier 1911, la Commission a désigné, pour le remplacer, M. l'Ingénieur des mines Ad. Breyre, à Bruxelles.

At the general meeting of May 3, 1906, the Congress ratified the section's decision as follows:

"The Sixth International Congress for Applied Chemistry, held in Rome in 1906, recognized the necessity of unifying the testing methods with a view of ascertaining the mechanical and technical stability of explosives and ratified the election of a special commission to study the question and submit a proposal to the next congress."

As a consequence of that resolution, the following program was adopted at once during the same congress:

First of all, to make inquiries in order to ascertain what are the existing methods in the various countries and to let them know to the Commission's members.

To gather the members' proposals with regard to the methods it would be suitable to adopt, be it that any existing method be recommended or that a new process be submitted for approval.

Finally to endeavor to secure an agreement on one system only.

In order to insure the realization of the first part of the program, the Standing Committee (at the time composed of Messrs Watteyne and Stassart) sent a letter to the Commission's members, asking them to let them know what testing methods are in use in their respective countries.

The answers, together with some other indications, have constituted a *first report*, dated 25 March, 1908, which was distributed to the members of the Commission and to other persons who were deemed in state to intervene usefully in the study of the question.

By some other letters the members of the Commission were then asked to let know and to explain their proposals about the methods which, in their opinion, were to be adopted uniformly in the different countries.

The replies have been gathered in a *second report* and were to form a basis for the final discussion and, if possible, a definitive agreement had to take place at the London Congress.

But, owing to the following circumstances, this final agreement was delayed:

Between the two Congresses the German government had studied the same question of the tests to be undergone by explosives for admission to rail conveyance and, precisely, among the persons entrusted with this study, were two of our colleagues, the Professors Will and Lenze.

Their studies lasted almost till the beginning of the London Congress, and the result was the proposal of a series of tests to apply to explosives of all classes.

This program or, rather, this regulation, the result of thorough researches and careful elaboration, deserved to be taken into consideration by our Commission and it has been thought advisable to wait till the said regulation had been in use in Germany for some months, in order to ascertain its advantages and its drawbacks. After such an experience, the International Commission would have to their disposal a fresh and important material and would so be in a position to decide with a better knowledge of the case.

Under these circumstances, all that the Commission could do was to suggest the postponement of their mission till the following Congress.

This proposal was carried at the meeting of the explosives section and later at the general meeting of the Congress on 2d June, 1909.

We do not think it necessary to reproduce the first reports, as these, condensed, made up to date and concluded by a project of conclusions elaborated by the Committee, have been made public enough thanks to their insertion in the publications of the Congress. Let us add that the Commission's works till 1909 have been published in the "Annales des Mines de Belgique" (t.XV 1909,—4th number) by Messrs Watteyne and Stassart under the title "Mines and Explosives at the Seventh International Congress of Applied Chemistry—London, 1909" (see pages 90 to 170 of separate copy).

This notice, which can be considered as a *third report* of the commission includes also (pages 170 to 182) Messrs Kast's, Will's and Lenze's notes on the work of the German commission. These notes have been submitted to the London Congress.

A schedule to the said notice by Messrs Watteyne and Stassart contains (pages 221 to 232 of "Annales des Mines de Belgique") a French translation of the new German regulation's principal part.

In conformity with the resolutions of the Congress, the commission waited till a sufficiently long time had elapsed to allow the German regulations' advantages and drawbacks to become apparent; then the committee (Messrs Watteyne and Breyre—the last gentleman having been appointed secretary in the place of deceased Mr Stassart) wrote in 1911 to the German members of the commission, asking them what observations had been suggested in Germany by the application of the new regulation.

Messrs Bichel, Heise, Will, Mente and Lenze (these last three members replying collectively) replied respectively on 29th September, 28th October and 7th November, 1911.

A letter dated 12th March 1912, issued by the Committee communicated the German colleagues's observations to all members, submitting at the same time to the Commission a new ante-project of conclusions.

This ante-project forms, together with Messrs Bichel's, Heise's, Will's, Mente's and Lenze's notes, the first schedule to the present report. It established a simplified classification based on the general peculiarities of the explosives with regard to their resistance to the causes of danger during conveyance and when stored. It also suggested to establish a limited number of tests applying to the various categories and after the results of which all explosives would be put in one or other of these categories. A first test applying to all explosives would allow to eliminate at once all defective products.

There was a rough indication of those types of explosives that would be classed in the three suggested categories.

As *Schedule I* gives the said project "in extenso" we do not think it necessary to say more about it here.

At the end of the letter dated 12th March the Committee asked the Commission's members to formulate without delay their observations on the subject and, at the same time, the Committee communicated to the members the wish of some of their colleagues to promote a meeting in a central part of Europe in order to allow the Commission to discuss and to get a definitive agreement with regard to the report to be submitted to the Washington-New-York Congress.

Most members replied [Messrs Will, Mente and Lenze (collectively), Heise, Barthélemy, Jacqué, Vitali, Spica, Lundholm] and Paris was selected as the seat of the meeting. The Committee wrote on 18th May 1912 (*Schedule II*) to the members, communicating these replies and calling a meeting for the 24th June at Paris in the premises put to our disposal by Mr Barthélémy.

In the mean time the Committee received further communications from the members:

1°) A letter from Mr. Gey van Pittius, who was prevented to take part to the Paris meeting by his staying in the Netherland's Indies. He wrote from Malabar on the 27th April 1912 (*Schedule III*).

2°) A further letter from Mr Lundholm, dated 10th June, 1912 (*Schedule IV*).

3°) A further note, dated 22nd June, from Mr Jacqué (*Schedule V*).

On the 24th June 1912 we met at Paris where we were the hosts of our colleague Barthélémy.

The following members were present at the meeting:

Messrs Watteyne, president, Barthélémy, Jacqué, Vitali and Will, members, and Breyre, secretary, were also present at the meeting: Messrs Mente (Mr Will's fellow worker) Bergassessor Beyling, Director of the testing station in Westphaly, deputed by Mr Heise, and finally, Mr Schmerber, engineer at Paris, who kindly acted as an interpreter.

Messrs. Bichel, Gey van Pittius, Heise, Lundholm and Spica had written that they were prevented to come to Paris.

After an arduous discussion, the most important features of which are reported in the meeting's account (*Schedule VI*) an agreement took place on the essential points of our resolutions as given below.

The real work of the Commission can be divided in fact in two periods: that of 1906 to 1909 and that of 1910 to 1912. The first three reports already published give an account of the first period's work; the work of the second period forms the matter of the schedules to the present report.

We beg to refer to these documents for the justification of the following conclusions.:

CONCLUSIONS

The result of the interchange of ideas and of the discussions which took place between the members of the Commission, is that it is impossible at present to solve *completely* the problem of unificating the testing methods of explosives, *i. e.*, that an effort to adopt at present uniform and exclusive regulations for all countries, would meet with insuperable difficulties.

Among these difficulties let us name the multiplicity of explosives, the conditions and necessities which are different for each country and the fact that most testing methods at present in use do not apply equally to all explosives.

But we think that it is possible to take an important step towards the solution and that it would mean a notable improvement on the present state of things would it be possible to choose, between the numerous tests now in use and which are different in the various countries, a reduced number of well defined tests which it would be easy to uniformly carry on and which would be sufficient to divide all explosives into some great classes having identical general peculiarities.

It is that selection the Commission has endeavoured to make, leaving to each government to adopt these principles to their own regulations under such conditions as they may think convenient.

The adoption of these selected tests would be a serious progress even for those governments who would only adopt them only as "consignation tests" maintaining at the same time their own process and uses, as it would introduce into the administration's requirements some marks which, later on, would grow in number and in this way bring the regulations nearer and nearer to the desired uniformity.

First of all, the commission decided to restrict their action to the "industrial" explosives, leaving out the explosives for shooting and war uses.

It follows that in the suggested tests the explosives having nitrocellulose as an important component, are not to be considered. Also the detonators will be left out, as they form a well distinct class in all countries.

A general observation is to be presented previously, it refers to the "*packing.*"

The commission draw to this important matter the attention of all governments: the question of security of conveyance cannot be separated from that of the mode of packing as it is thanks to a suitable packing that the dangers of many explosives can be so nullified that they can be carried with security.

It would be easy to uniformise the regulations on packing and this point must be commended to the best attention of the governments.

The three tests the commission think it advisable to commend for international adoption are the following: The first tests applies to all types of explosives and would allow to distinguish at once those explosives the conveyance of which would be dangerous; the following tests would show the shock, friction and fire (to various degrees) resisting properties and so lead to a simplified classification of explosives after their properties.

I PRELIMINARY TEST

Two samples (of ten grams each) of non dessicated explosives are put into a glass capsule fitted with a cover (that cover being simply put over the capsule) and having a diameter of 35 m.m. and a height of 50 m.m. The samples are then put into a stove heated to 75° C., where they remain for 48 hours. No discomposure nor notable modification in aspect or smell must have to take place. The azotized explosives must let out no rutilant vapors.

II SHOCK RESISTING TEST

This will consist in a testing of equal weights of pulverized and dessiccated explosive for one part and of pure, pulverized and dry picric acid for the other part with the same apparatus and under identical conditions. The samples of 5 to 10 centigrams each will be put on a steel anvil so as to form a coat of about 1.27 c. m.(½ in.)

diameter. On this coat of explosive is put a steel cylinder with a diameter of 1.27 c.m. and same height. Each explosive must undergo 10 consecutive tests with a view of determining the average fall height at which an explosion takes place.

To be considered as shock resisting the explosives must resist to at least the same shocks as does pure pulverized picric acid.

N. B.—To carry on this test may be used either the English free fall apparatus or those described at the Sixth International Congress of Applied Chemistry (Rome 1906).

It is to be noted that for this test as well as for the following one it is not necessary for the "modus operandi" to be strictly uniform; the use of the "comparison explosive" viz. picric acid insures the results to be constant but in any case picric acid must be tested in strictly the same way and with the same apparatus as were the other explosives.

II B. FRICTION RESISTANCE TEST

The explosives must be put in an unglazed china mortar, slightly heated (20 to 30° C.) and must be at least as friction resisting as pure pulverized picric acid when undergoing identical test in the same apparatus.

III FIRE RESISTANCE TEST

a) FUSE TEST. *Three grams of pulverized explosive are poured in a glass tube: through slightly shaking the stuff gets a well even surface. Then a slowly burning fuse (1 c.m. per sec.) is introduced into it. The test must be repeated twice.* Those explosives that catch fire are classified as deflagring powders or easily inflammable explosives.

b) RED-HOT IRON CAPSULE TEST. Those explosives that will have undergone the previous test without catching fire will be submitted to a high temperature test with a view of ascertaining their ability to explode when exposed to fire. *An hemispheric iron capsule of 12 c.m. diameter and 1 m.m. thickness is put on a burner till it gets red hot: then a small quantity (0.5 gr.) of pulverized explosive is poured into it. If no detonation takes place the quantity is augmented till 5 gr. This test must be carried on three times.*

c) HOT IRON TEST. Its purpose is to ascertain the unaptness of safety explosives to catch fire.

After some preliminary tests on small quantities in order to ascertain first that the explosives have relatively little propensity for catching fire, 100 gr. of explosive are put on an amianth plate; the stuff is then put in contact with the extremity of an iron bar (diameter 15 c.m., length 10 c.m.) heated to cherry red (about 900° C.). The stuff must burn slowly without any explosion and the fire must die out as soon as the iron bar is taken away.

In consequence of the three advocated tests, all explosives are distributed into three clasess:

Those explosives that are sensitive to shock will give, when undergoing test II–IIb, inferior results to those given with picric acid and so they will form a first class (dynamites, some chlorate explosives and explosives of similar character).

As a result of test IIIa, there will be a second class comprising those explosives that explode when put in contact with the burning fuse or that catch fire (especially the various deflagrant powders).

The combined test II b and c will put aside a third class: those explosives that are sensitive neither to shock nor to fire and that can be conveyed with an almost absolute safety.

Should some explosives after having undergone with success test II–IIb and test III a, explode when undergoing test IIIb (hot capsule test); they would have to be put into the first class, but it seems that this would only occur with a few explosives of a rarer type.

In the event of some explosives having been successful when tried with II–II b, IIIa, and III b tests, and burning with some violence when undergoing test III c, it would be necessary to place them in the second class (powders) or to let them form an intermediary class between the second and the third class.

In presenting their conclusions as above to the Eighth International Congress of Applied Chemistry, the members of the Commission consider that their task is fulfilled. They beg the Congress to express a wish that would be transmitted to the various interested governments, that an international convention be formed, with official powers, in order to bring the work to conclusion by getting an international agreement on those questions that are connected with that of international conveyance of explosives (tests, packing, classification etc.).

For the Commission

The Secretary,
AD. BREYRE.

The President,
V. WATTEYNE.

(*Résumé*)

RAPPORT SUR LES PROPRIÉTÉS DES CIMENTS PORTLAND ARTIFICIELS BELGES

ROBERT ADAN
Ghent, Belgium.

Un relevé analytique des essais opérés en cours de fabrication des ciments pendant les trois dernières années écoulées permet de se rendre compte des qualités des ciments Portland artificiels belges.

Le travail montre qu'il n'existe pas de rapports entre la densité spécifique, la perte au feu, la finesse de mouture, la vitesse de combinaison et la propriété de résistance des ciments.

Alors que le poids, la densité et la finesse de mouture varient peu, en étudiant les conditions de résistance après 28 jours on constate que les valeur de traction et de pression sont ascendantes.

Le travail établi les rapports existant: a) entre le poid du volume, la densité du ciment sec et la perte au feu, b) entre la perte au feu, la quantité d'eau nécessaire pour le gâchage et la finesse de mouture, c) entre la perte au feu et le résidu au tamisage, d) entre la cohésion et la résistance.

Il montre les effets du vieillissement sur le poids, la perte au feu, la quantité d'eau employée et la finesse de mouture; il établit la différence de résistance entre les briquettes en pâte de ciment pur et les briquettes en mortier et il prouve aussi leur résistance.

THE FUNCTION OF THE VARIOUS RAW MATERIALS IN A SHEET STEEL ENAMEL

ROBERT D. LANDRUM
Canandaigua, N. Y.

An enamel, such as is used on cooking utensils, is a glass of such nature that it will adhere to steel and on account of this, its composition is more complicated than that of ordinary glass. The materials used to make ordinary glass are sand, limestone and soda ash, with lead oxide added to certain types. These glasses, however, will not adhere to iron and have a co-efficient of expansion entirely different from that of sheet steel, and also the temperature at which they must be melted would soften the steel shape. An enamel, then, although a glass in every sense of the word, and containing the elements introduced by these glass materials, also contains others added to modify the physical properties and to suit it for the purpose intended.

QUARTZ AND FLINT

Sand is the material which furnishes silica (SiO_2) to glass and it is sometimes used in enamels. However, enamels must melt at a much lower tempertaure than glass and thus require the silica-furnishing material to be very finely powdered in order that it may combine with the other materials at this lower temperature. As it is more expensive to pulverize sand than it is to pulverize quartz or flint, one of these minerals—each having the same chemical composition as sand—is generally used.

It may be taken as a general rule that other things remaining constant, the higher the per cent of silica the higher will be the melting point of the enamel and the greater its acid resistance. Silica also has a low co-efficient of expansion and increasing it in an enamel lowers the co-efficient of expansion of that enamel. Therefore, one method of regulating an enamel coating is to *increase* the silica when the enamel is inclined to split off when cooling after muffle burning. This remedy is indicated when the curve of the enamel chips, showing that the enamel contracts less rapidly on cooling than the iron.

SODA ASH

In glass, all of the sodium oxide is introduced as soda ash, while in enamel, this material is only used when it is desirable to add the sodium oxide without the introduction of any other ingredient.

Up to a certain point the addition of silica to an enamel formula may lower the melting point. An exaggerated example is that Calcium Oxide (lime) alone is practically infusible, but on adding silica, a fairly easily fusible glass is formed.

Soda Ash is commercially pure anhydrous sodium carbonate (Na_2CO_3) and, therefore, besides adding the sodium oxide to the finished enamel, gives off carbon-dioxide gas during smelting and the melted mass is then quite thoroughly stirred by the evolution of this gas and many impurities are carried off.

The function of the sodium oxide is to combine with the other materials (especially the silica) and form a vitreous product. The larger the proportion of sodium oxide (in comparison with the amount of silica present) the lower will be the melting point of the product and the less resistant to acids it will be. At the same time, however, an increase of the sodium oxide tends to make the product more flexible and less brittle.

Many enamels do not include soda ash in their batch mix formulas as sufficient sodium oxide is furnished by the feldspar, cryolite and borax.

FLUORSPAR AND CALCITE

Fluorspar and Calcite are the minerals which are used to supply the lime (CaO) to enamels. In glass, limestone furnishes this important ingredient, but on account of the impurities, always present in this mineral, it cannot be used in the more carefully compounded enamels. Both Fluorspar and Calcite have their advantages and disadvantages and, as their cost is about the same, a careful consideration of these is necessary before one can decide which is the better to use in an enamel. American practice is inclined to favor the use of Fluorspar.

FLUORSPAR

The calcium present in Fluorspar seems to combine more easily with the other ingredients of the enamel batch than does the calcium oxide of calcite. This is evident from the fact that Fluorspar enamels melt at a lower temperature and become homogeneous in a shorter time than calcite enamels. In enamels, which derive some of their opacity from cryolite, this is of particular advantage, for it is a well known fact that the longer a cryolite enamel is smelted, the less opaque it becomes.

The disadvantages pertinent to the use of fluorspar instead of calcite in an enamel formula are due to two things; this mineral contains fluorine and is a powerful reducing agent at the temperature attained in the smelter. The fluorine is set free during the smelting and, although the virtues of fluorspar are very likely due to the energetic action of this element, it is also active in corroding the furnace linings and the life of the smelter is shortened.

The reducing action of this mineral makes it very necessary to carefully regulate the smelter so that the atmosphere is always oxidizing and where a large amount is used the percentage of nitrate in the batch mix must be increased.

CALCITE

Calcite in enamels does not act as a reducing agent nor does the gas given off by it (CO_2) attack the furnace linings. Therefore, the life of the smelter is longer and there is no necessity for adding more nitrate nor of so carefully controlling the atmosphere of the smelter.

The disadvantages common to a calcite enamel are due to its requiring a higher temperature and a longer time to combine with the other ingredients of the batch. With cryolite enamels, this longer smelting is certain to cause them to lose some of their opacity.

DEFECTS CAUSED BY FLUORSPAR AND CALCITE

Unless sufficiently smelted and thoroughly oxidized, fluorspar enamels are not stable and, on standing, lose their gloss, while calcite enamels, unless smelted entirely homogeneous and free from carbonate, are inclined to chip and scale and to form bubbles and blowholes where the enamel is applied thickest.

CALCIUM OXIDE (CaO)

The calcium oxide introduced by either of these materials will replace sodium oxide in an enamel formula and, while not affecting the melting point to any great extent, makes the enamel much harder, more acid resistant, more glossy and more opaque. Calcium oxide increases the brittleness of an enamel, however, but at the same time it allows the addition of more boric anhydrid and this ingredient counteracts this effect.

FELDSPAR

Feldspar is generally included in the batch mix of any enamel. The new element introduced by this material is aluminum in the form of alumina (Al_2O_3). It also adds sodium oxide (Na_2O) or potassium oxide (K_2O) or both and at a much cheaper price per pound than they can be bought in any other form.

The other ingredient introduced by feldspar is silica (SiO_2) and it is likely that *its* introduction *thus* has the advantage over its introduction as quartz or flint, in that, in feldspar, nature has already combined the alumina and the silica. An enamel, therefore, getting its silica from feldspar requires less heat in smelting than one getting the silica otherwise.

The alumina added by the feldspar makes the glass softer and also less resistant to acids, but when other suitable ingredients are present, causes the enamel to become translucent. It also lessens the tendency of the enamel to chip but makes it more liable to craze. It combines directly with the other ingredients forming a homogeneous product and, therefore, does not aid in improving the stretching qualities of the product as does the alumina added as clay, which material will be taken up later.

BORAX AND BORIC ACID

One of the most characteristic ingredients of an enamel is boric anhydrid (B_2O_3) and this is furnished to the batch mix by borax or boric acid, Borax is generally used for this purpose, as it is much cheaper and the only enamel in which its use is prohibited are those whose full quota of sodium oxide is furnished by the feldspar and cryolite. Borax contains 16% of sodium oxide, so in such enamels, boric acid ($B_2O_3.3H_2O$) would be used.

Boric anhydrid (B_2O_3) makes the enamel more elastic, less brittle and changes the co-efficient of expansion in such a way that the glass produced may be used on steel. It is like the silica in many ways, increasing the acid resistance and allowing more alkalies and metal and earth oxides to be used in the mix and like silica causes the enamel to chip when present in excess.

Unlike silica, however, it increases the viscosity of the smelted enamel and lengthens the period between the temperature at which the enamel will melt to form a homogeneous vitreous coating and the temperature at which it will "burn off," thus making the enamel less liable to be spoiled by poor shop practice.

This property of viscosity, which the boric anhydrid increases, causes the enamel to remain thick and gummy on the black shape, while being heated in the muffle, instead of getting thin and running off as would ordinary glass.

CLAY

Clay is always used in the mill mix of an enamel that is to be slushed on wet and is sometimes included in the ingredients that go into the smelter. In the latter case, it is used to introduce alumina and silica, as does feldspar, but without introducing any alkalies. Clay is quite infusible and very finely divided, thus adding opacity to the enamel. When added at the mill, it gives besides the qualities already mentioned plasticity to the wet enamel and holds up the glass particles during slushing. It also causes the powdered glass particles to adhere to the steel shape during the drying before muffle burning.

Whether added at the mill or in the smelter, clay adds to the stretching qualities of the finished enamel coating. This is accounted for by the infusibility of the clay, which property keeps it from entering into complete combination with the other materials. Instead, it holds the glass masses (with which each particle of clay is surrounded) apart during the contraction of the steel and allows them to pull away from it without chipping during expansion. Under the microscope, enamels with a high clay content are very porous—the higher the clay the more porous—and, therefore, clay in an enamel always lessens the gloss. This is the prime factor in limiting the amount of clay that can be used in an enamel.

STELLMITTLE

The plasticity of clays in water can be greatly increased by adding to the water very small quantities of acids, bases or salts which dissociate in the water. These cause the clay to assume a colloidal form quite jelly-like in nature and thus make the enamel batch in which they are present much thicker without removing any of the water.

These are called "Stellmittle" or fixation materials by the German enamelers. Any acid will answer, but, as the effect on the finished product is deliterous, these are seldom used. *Borax* (a saturated solution in hot water) or a mixture of this with a saturated solution of sodium carbonate is generally used in ground coat enamels and may be used in small quantities in white enamels. *Magnesium Sulfate* has much favor with most enamelers and its principal virtue is that less of it is required than of any of the others. Magnesium sulfate cannot be used in the ground coat, as it will cause the iron to rust.

Magnesium Oxide and Carbonate are used in the mill mix and are good for this purpose, as also is ammonium chloride, ammonium carbonate and ammonium acetate. Some enamelers also use the sulfate of sodium but any of the sulfates will impair the gloss of the product.

OXIDE OF TIN

Tin oxide is one of the most important and, at the same time, most expensive of the enameling materials. Indeed a French writer defines an enamel as "an opaque glaze containing tin oxide."

Added to the smelting batch up to about 3% of the stannic oxide—the commercial oxide of tin—is reduced to stanous oxide, which forms a transparent compound with the silica. All over 3%, and practically all added at the mill, remains in suspension in the enamel, and, keeping its intense white color, makes the enamel opaque.

The writer has used as high as 30% of this material in an excellent, though costly, enamel but the amount used in white enamels for cooking utensils seldom runs below 5% or above 15% in the finished product.

All efforts to entirely replace this material with a cheaper one have led to the conclusion that some oxide of tin is absolutely necessary in a white enamel. Other materials can replace part of it, but the question as to whether there is any actual saving in so doing is a matter of dispute.

The higher the percentage of tin oxide in an enamel the thinner it may be applied and attain a given standard of whiteness. This thin application reduces the production cost in two ways, viz., less enamel is required and the number of seconds, caused by the scaling off of the too thick coatings, will be greatly reduced. But of still more importance is the fact that the thin application of the enamel adds greatly to the durability of the ware under punishment both by impact and by sudden changes of temperature, thus adding to the reputation of the manufacturer. Then too, the opacity produced by this material is practically "fool proof." The tin oxide substitutes must be handled with the greatest of care during every operation and the slightest variation of method of procedure is likely to spoil the enamel.

CRYOLITE

The only material which produces opacity besides the tin oxide and which has stood the test of time is cryolite. This material must be added in the smelter and although it adds no new elements those added are so geologically combined that at a certain temperature they make the enamel frit quite translucent and even opaque when thickly applied. The amount of this material which can be used in a given enamel is limited by the large amount of sodium oxide which it introduces. Cryolite is a double fluoride of aluminum and sodium and in the enamel about 20% of its mass escapes as fluorine gas and is replaced by oxygen. Thus it is very necessary to keep the atmosphere of the smelter oxidizing, and this is best done by having sufficient nitrate present in the enamel batch. The opacity produced by cryolite is quite elusive and the greatest care must be taken to have the temperature, both of the smelter and the muffle furnace, right and the length of time for smelting and burning correct.

OXIDE OF ANTIMONY

Antimony Oxide is another substitute for tin oxide and like cryolite this is added in the smelter. Antimony-containing enamels are quite opaque, if applied in thick layers; thin coats of such enamels, however, are quite transparent and it is doubtful whether or not antimony has any great coloring effect on a properly applied enamel. Antimony oxide is in itself quite poisonous and when used in quantities large enough to give the desired opacity, there is a danger that some of it may be made soluble in the cooking acids and thus be detrimental to the health of the consumer. In practice most antimony enamels contain less than 5% of this material.

Both antimony and tin oxide and, in fact, all metallic oxides add luster to the enamel coating, for they increase the density and it has been shown that the gloss of a glass or enamel increases directly with the density.

ZINC OXIDE

The oxide of zinc is the only metallic oxide, except that of tin, which can be safely added to a white enamel for the purpose of increasing its luster, and even it will lower the resistance to corrosion by acids of such an enamel very markedly.

Used in large quantities and in very soft enamels it produces some opacity. Its main use, however, is as a substitute for the objectionable lead oxide in formulas for colored enamels. Like lead, it has the property of making such colors more brilliant.

SALTPETER AND CHILI SALTPETER

Potassium nitrate (saltpeter) or sodium nitrate (Chili Saltpeter) is used in enamels, which require oxidizing agents in the smelter.

Oxidizing agents are necessary in enamel formulas which contain fluorspar or cryolite to replace the fluorine given off in the smelter and also in white enamels containing iron as an impurity. In the latter case, they change all of the iron to the higher oxide which has a less intense coloring action on the enamel.

Soldium nitrate is much cheaper than potassium nitrate but must be stored in air tight containers as it is very deliquescent. The impracticability of storing the material has forced manufacturers to use the more expensive nitrate or to employ a chemist to make daily determinations of its moisture content. Then too, experiment has shown that the presence of potash in an enamel already containing soda tends to increase the gloss and to lower the melting point without affecting the other properties. This would be a reason for using nitrate of potash instead of nitrate of soda in an enamel, in which potash is not supplied by some other material, for potassium oxide remains from the saltpeter, while sodium oxide remains from the Chili saltpeter.

MANGANESE DI-OXIDE

Manganese do-oxide (MnO_2) is a strong oxidizing agent and its use in enamels is primarily due to this fact. Used in an enamel batch, it disintegrates during smelting into manganous oxide (MnO) and oxygen gas and the latter, besides stirring the molten enamel, changes some of the ingredients to their highest possible oxides.

This action is especially desirable in ground coats which must stand a hot fire in the muffle, as it renders over-burning during this operation less probable.

Manganese compounds cannot be used in white enamels in more than minute quantities as it colors the glaze an amethyst purple. Its second use in enamels is due to this coloring action and it is used in many colored enamels.

OXIDE OF COBALT

Oxide of Cobalt (CO_3O_4) is added to enamels either to give them a blue color or to make them adhere directly to the steel. For the second reason, all successful ground coats contain oxide of cobalt. An enamel may be so compounded that its co-efficient of expansion will be exactly that of the sheet steel upon which it is to be used, and, yet without the addition of oxide of cobalt, according to the writer's experience, it cannot be made to adhere to the steel as well as with this addition. There are many theories as to the exact function of cobalt in a ground coat enamel and the popular one at present, is that silicate of cobalt in the enamel frit is reduced during muffle burning to a lower silicate and perhaps to metallic cobalt. The oxygen, which is given off in either case then unites with the iron of the black shape and is taken into the enamel as ferrous silicate and, if metallic cobalt is left, this unites with the iron of the black shape, forming a widely distributed porous alloy. At any rate, there is an interaction between the cobalt of the enamel and the iron of the black shape which binds the enamel to the steel. Whether this is the correct explanation of the action, we do not know, but it is certain from practical experience that the cobalt-containing ground coat enamels are more easily burned correctly by the men in charge of the muffle furnaces. This is explained by the fact that there is a definite, though delicate, color change from blue to green in cobalt-containing ground coat enamels at just the point at which the enamel so fired will adhere most firmly to the steel coat. Such an enamel, when correctly burned, will have a very characteristic greenish tinge; when under-burned a blue color, and, when over-burned, a brownish black color.

ETHYL ETHER BY CATALYSIS

CHARLES BASKERVILLE
College of the City of New York, New York, N. Y.

Sabatier and Mialhe[1] have shown that several metallic oxides (thoria, alumina, and tungsta) exercise a "catalytic action" on alcohols between 300° and 350° C. It would appear from their investigations that this action is almost entirely that of dehydration with the separation of ethylene, although when operating at a lower temperature, the dehydration is said to be incomplete and to be capable of limitation to the production of ethyl oxide.

The dehydration of ethyl alcohol in the presence of thoria has been studied in this laboratory[2] and the results obtained show some variance with those of Sabatier and Mialhe. The contributions of these authors are not very explicit as to experimental details, but we endeavored to observe all the conditions necessary for the production of ethyl ether by partial dehydration, according to the reactions:

$$2CnH_2n+1OH+ThO_2=H_2O+ThO(OC_2H_2n+1)_2;$$
$$ThO(OCnH_2n+1)_2=ThO_2+(C_2H_2n+1)_2O.$$

The apparatus used in our experiments, illustrated herewith, consisted essentially of a jacketed porcelain tube containing glass beads covered with pure thoria, heated in a combustion furnace, and over which vaporized absolute ethyl alcohol was conducted by means of a purified air current. Suitable means were provided for recovering products of dehydration and oxidation, and excess of ethyl alcohol was absorbed in water kept at 40° C. No difficulty was experienced in maintaining the desired temperatures throughout the train of apparatus.

In experiments 1 (length, 1 hr. 20 min.; average temperature

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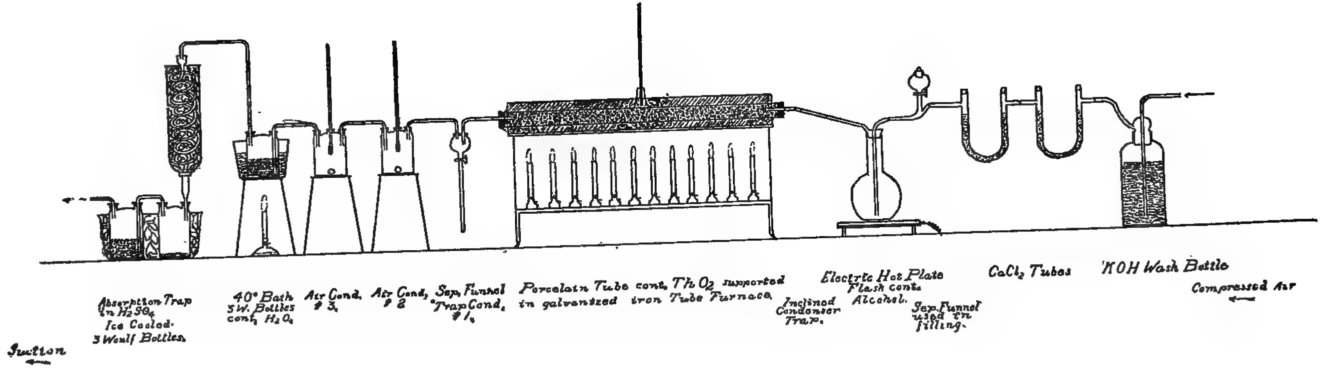
[1] Compt. rend., *150*, 823. See also *Idem*, *149*, 995; *150*, 1217; *151*, 359, 492.

[2] The experimental work was carried out by Messrs. Barnett Cohen and Alfred V. Salamon.


Suction
Absorption Trap in H_2SO_4 Ice Cooled. 3 Woulf Bottles.
40° Bath 3 W. Bottles cont. H_2O_2
Air Cond. # 3.
Air Cond. # 2
Sep. Funnel Trap Cond. # 1.
Porcelain Tube cont. ThO_2 supported in galvanized iron Tube Furnace.
Inclined Condenser Trap.
Electric Hot Plate Flask cont. Alcohol.
Sep. Funnel used in filling.
$CaCl_2$ Tubes
KOH Wash Bottle
Compressed Air

245° C.) 2 (2 hrs. 45 min.; 233° C.), and 3 (5 hrs. 15 min.; 228° C.), in all of which 375 cc. of ethyl alcohol were used, no reliable results were obtained, although it was found that the ethyl alcohol had evidently undergone oxidation.

In experiment 4, in which 390 cc. of ethyl alcohol was used during 3 hrs. 20 min., and in which the thoria tube was maintained at 150° C., a small amount of a heavy yellow oil condensed in the tube leading from the thoria tube, and it was found that this formed at about 200° C. The sulphuric acid, kept in absorption bottles in ice at the end of the train, became discolored, but no indications of the formation of ethyl ether were had. On the conclusion of the experiment, the thoria was found to possess a brownish black color and fruity odor, but upon ignition in air it regained its original color, and this revivified thoria was used in the following experiment.

In experiment 5, the time of the run was 4 hrs. 30 min., and 390 cc. of ethyl alcohol were passed over thoria heated to 245° C. During this experiment tests were made for the formation of ethylene[1], and indications were had of the presence of unsaturated hydrocarbons and carbon dioxide in the gas issuing from the last sulphuric acid bottle. Upon the conclusion of the run, the first trap was found to contain a very small amount of ethyl ether, and the sulphuric acid at the end of the train was darkened and had a pungent ethereal odor. The water solutions in the baths maintained at 40° C. for the absorption of alcohol were fractionated; considerable amounts of acetaldehyde were found, also small amounts of acetic acid.

In experiment 6, the average temperature was 253° C. and the period of the run was 3 hr. 25 min. Care was exercised to establish the dehydration observed by Sabatier and Mialhe, and the formation of ethylene and carbon dioxide was shown; however, the amounts formed were small under the conditions of the experiment. No ethyl ether was found in the traps, receivers or absorption vessels, but the heavy yellow oil noted in experiment 4 was again found this time being condensed in the receivers. Not sufficient of this oil was obtained for examination. The alcohol absorption vessels were found to contain an alcohol solution giving a strong acetaldehyde reaction.[1]

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[1] By means of iodine and starch solution, bromine water, and palladium chloride solution (see Phillips, Am. Chem. J., *16*, 4, 266).

The above experiments warrant the conclusion that, under the experimental conditions described, no satisfactory yield of ethyl ether is obtained in the neighborhood of 250° C. It is planned to extend these experiments, using other rare-earth oxides and working at lower temperatures.

[1] The acetaldehyde present was of such an amount as to lead us to believe that it did not arise from the autoxidation of the ethyl alcohol which originally contained but a mere trace of acetaldehyde. The water solutions were carefully stored up to the time of fractionation.

CHEMICAL TREATMENT OF WASTE WOOD

H. K. Benson
Professor of Industrial Chemistry in the University of Washington, Seattle, Washington.

In the states comprising the Pacific Northwest of the United States the extent of the land from which the forests have been removed is measured in millions of acres. In the western half of the state of Washington alone the logged off or cut over land comprises approximately three million acres. Upon this land there still remains for the most part a dense and tangled mass of debris from the logging operations consisting of stumps, tree tops, branches, rejected logs and underbrush. To remove this debris and clear the land so that it may be used for agriculture requires an outlay of labor and power which, when measured in money, is equivalent to not less than $100 and frequently as much as $200 per acre.

In view of these facts it has seemed reasonable to many that an attempt should be made to utilize this waste by subjecting it to proper methods of treatment so as to yield marketable commodities and thus render some compensation to those engaged in clearing, thereby lessening the cost of the agricultural lands of the wooded portions of the Pacific Northwest. With this end in view a number of investigations have been carried on by the writer in cooperation with the Federal bureaus and with commerical organizations and an attempt will be made in this paper to present a review of the work which has been under way during the past three years. This may be conveniently grouped under the heads of (1) Steam distillation products; (2) Destructive distillation products; and (3) Hydrolyzed or fermentation products.

I. STEAM DISTILLATION PRODUCTS

The work has thus far been largely restricted to the waste wood resulting from the logging of Douglas fir (Pseudotsuga taxifolia)[1] and comprises the products obtained by distilling fir stumps in one experiment and fir boughs containing the needles in the other experiment.

For the distillation of fir stumps one of the commercial plants was utilized. A representative sample of wood was transported to the plant and there reduced by means of a wood chipper or "hogging" machine to small chips. Four thousand pounds of these chips were loaded into a retort and steam distilled for a period of four hours, the steam being obtained from boilers operating under a pressure of fifty pounds.

The yield of oil obtained in this experiment was five and one-fourth ($5\frac{1}{4}$) gallons. It had a straw yellow color with a specific gravity at 15.5 degrees C. of 0.8799 and a viscosity (Engler method) of 1.13. When redistilled with saturated steam it yielded eighty per cent of water white distillate, the residue consisting of a heavy yellow oil with a characteristic but pleasant resinous odor. The name "Oil of Douglas Fir" has been tentatively assigned to this residue.

The water white distillate was next examined by the methods prescribed in Bulletin 109, revised, Bureau of Chemistry, United States Department of Agriculture, and the following constants determined:

Specific gravity at 15.5° C.	0.8676
Distillation—Initial boiling point is 156° C. and 95% distills between 156° and 165° C.	
Residue on evaporation	1.115 gms.
Refractive index at 15.5° C.	1.4718
" " " 20° C.	1.4696
Polymerization	less than 0.1 cc.
Flash point	46° C.

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[1] A detailed study of the oil obtained from the leaves or needles of the Western Red Cedar (Thuja plicata) has been made by Rose and Livingston in J. Am. Chem. Soc. *34201*.

Spot test	no stain
Rotation (∝) 20° C.	25° laevo
Iodine number	211.9

These results show that the water white distillate conforms to the tests for turpentine and make it similar to that obtained from the Baltic pine in Europe and generally known as French turpentine.

The yellow residue or oil of Douglas fir was next studied in order to determine its nature and probable composition, and the following constants determined:

Specific gravity at 20° C.	0.936
Rotation (∝) 20° C.	37.6° laevo
Refractivity at 20° C.	1.4818
Solubility in 70% alcohol	49 parts oil in 100 of alcohol.
Acid number	1.55
Saponification number	11.1
Iodine number	185.0
Melting point (By solid CO_2)	below 40° C.

Distillation—Initial boiling point is 175°, 57.4% distilling between 214 and 226° C.

Combustion data	Hydrogen	11.9%
	Carbon	76.0%
	Oxygen	12.1%
	Nitrogen	00.0%
	Halogen	00.0%

From these results and others described by Benson and Darrin,[1] the conclusion was reached that at least one-third of the oil of Douglas fir consisted of terpineol and that it bore a close resemblance to the pine oil described by Walker[2] and Teeple[3] and for which important industrial applications have been found. Subsequent experiments have shown the terpineol content to be considerably higher, probably close to 48%.

For the steam distillation of green fir boughs and fir needles a small still in the chemical engineering laboratory of the University of Washington was used. From 100 to 200 pounds of

[1] J. *Ind. Eng.* Chem. *3*: 818.

[2] Mass. Inst. Tech. Bull. Sept., 1905.

[3] J. Am. Chem. Soc. *30*: 412.

green boughs after being cut into small pieces by a wood chipper were distilled for three hours with steam heated to 250° F. in a superheater. The yield of oil thus obtained was 0.45%. It had a yellow-green color with a decidedly pleasant odor. To this oil the name "Fir leaf oil" is tentatively assigned. Its specific gravity at 20° C. is 0.864 and on fractional distillation the following results were obtained.

162–168° C.	18% clear water white
168–172° C.	23% " " "
172–175° C.	18% " " "
175–180° C.	15% less clear, slightly yellow
180–230° C.	16% " " yellow
Residue	10% brown liquid

The chemical composition as found by combustion analysis is as follows:

C	78.3%
H	11.4%
O	10.3%

On more careful fractionation under diminished pressure it was found that 70% of the fir leaf oil boiled at the same temperature (65 to 70° C. at 20 mm) with a specific gravity of 0.8639 at 20° C., while the last fraction boiled between 70° and 200° C. at 20 mm. and has a specific gravity of 0.8905 at 20° C. It seems probable from the above results and from other incomplete data that fir leaf oil consists in the main of a terpene and an ester the nature of which is now being determined in the investigation under way, by the usual methods.

Before concluding this portion of the review it should be noted that the process of steam distillation of coniferous wood is often supplemented by extraction with a solvent in order to recover the resin usually present in wood of this character. No apparatus suitable for such extraction having been available, an attempt was made to ascertain the rosin content of the steam distilled chips which had yielded the water white turpentine and the oil of Douglas fir by percolating hot alcohol over the chips. The yield thus obtained was about 300 pounds calculated to a four thousand pound sample basis. This extract was dark brown in color, 70% of which was soluble in petroleum naptha (86° Be.) and upon removal of the latter yielded a lemon yellow solid of good transparency and clearness.

II. DESTRUCTIVE DISTILLATION PRODUCTS

In order to carry on these tests use was made of a number of industrial plants in operation in the Northwest, all of which, however, have been operating on the waste wood from sawmills. Stumpwood was therefore transported to a plant of the destructive distillation type and subjected to the usual process, the yield of products being given in the following table:

Amount of wood distilled	29,160 lbs.
Crude turpentine	12.5 gallons
Light oil	25.0 "
Heavy tar	93.9 "
Pyroligneous acid	1,314 "
Charcoal	5,547 lbs.

The refining of these products has not by any means become standardized in the Northwest and it is difficult to give in condensed form a statement of the exact products contained in the groups of products mentioned in the table of yields.

From the crude turpentine and light oil mentioned wood turpentine conforming to the usual standards for such turpentine can undoubtedly be obtained. The analyses made in this investigation show the need of methods of refining which differ from those now in use in the Northwest and modifications are being made with this purpose in mind.

The analysis of the tar, however, may be presented as indicative of its nature and consequent uses. These results are given in the tables which follow:

ANALYSIS OF TAR

Specific gravity at 18° C.	1.068
Flash point	105° C.
Fire point	131° C.
Free carbon	1.18%
Viscosity at 100° C. (Engler method)	1.5

Fixed carbon	3.16%
Insoluble in 86° Be'. naptha	24.37%
Distillation;	
Water	4.0%
Below 170° C.	8.0%
170°–215°	61.0%
Solid pitch	22.0%

ANALYSIS OF SOLID PITCH

Color—Black with bright lustre in mass and brown when powdered

Fracture	Conchoidal
Melting point	154° C.
Free carbon	18.23%
Volatile matter	68.28%
Fixed carbon	31.54%
Ash	0.18%

The results obtained from the analysis of pyroligneous acid are not of a sufficiently definite character to serve as a summation, in part due to the manipulation of the acid in the plant and in part to the methods used for analysis. Modifications, now in progress will, it is believed, give more accurate and conclusive results. From the incomplete data available a conservative estimate places the yield of products which may be obtained from the pyroligneous acid in the test under discussion as follows:

Methyl alcohol containing acetone	8 to 10 gallons per 4000 lbs. of wood
Gray acetate of lime	85 lbs. per 4000 lbs. ofwood.

In concluding the review on this process it may be said that the successful utilization of wood waste by destructive distillation depends upon the adoption of successful refining methods and the production of marketable commodities such as wood turpentine, shingle stain oils, tar paints suitable for damp proofing and for metallic surfaces, commercial acetic acid, wood alcohol suitable for denaturing purposes and briquetted charcoal fuel. This contemplates an interesting field but none the less imperative for the success of this process.

III. HYDROLYZED OR FERMENTATION PRODUCTS

The use of wood waste in the Pacific Northwest for the manufacture of ethyl alcohol under the Classen patents has been practiced during the past year at one plant. Sulphurous acid was used as the agent for hydrolyzing the sawdust which was obtained from sawmills. The investigations under the writer's direction were not directly concerned with this method of utilization and the yield of ethyl alcohol is not known except as reported by the officers connected with the plant who put the yield at 30 proof gallons per ton of theoretically dry sawdust.

The problem of the utilization of the extracted sawdust in this process was, however, made the subject of an investigation in the writer's laboratory. This material is of a dark brown color and granular in character when dry. It contains approximately 90% of cellulose and gives no reaction for ligno cellulose. The dark color may be removed by boiling with a 10% solution of nitric acid yielding a light or lemon yellow product which was found particularly adapted for conversion into pyroxylin and viscose products.

The future of this method of utilization is, however, quite uncertain at this time, since the single plant in operation has encountered many difficulties of a discouraging nature and at this time has ceased to use sawdust as its raw material for the manufacture of ethyl alcohol.

GENERAL SUMMARY

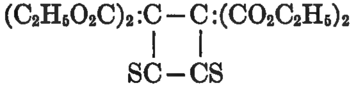
The waste wood of the Pacific Northwest is of enormous quantity. The experiments above cited show that high grade commodities may be obtained from this kind of wood by the various processes mentioned. The successful utilization, however, lies in the production of commodities which may be sold in somewhat locally restricted regions and the industries to be built up on waste wood as a raw material cannot therefore entirely follow the beaten path which similar industries have pursued in the more populous and congested centers.

(Abstract)

THE ACTION OF POTASSIUM XANTHOGENATE ON HALOGEN-MALONIC ACIDS

EINAR BIILMANN AND ERIK HOST MADSEN
Chemical Laboratory of the University, Copenhagen

In former papers it has been shown, that by action of potassium xanthogenate on the halogen derivatives of a series of organic acids there are formed xanthogenic derivatives of these acids, which by treatment with aqueous or alcoholic ammonia are converted without any difficulty into mercapto acids, these processes presenting a very convenient method for the preparation of pure mercapto acids.[1] By working with halogen derivatives of malonic acid and alkylmalonic acids, however, particular difficulties were observed. By action of the xanthogenate of potassium, e. g., on the diethyl ester of brommalonic acid, only the so called thiocarbonylmalonate of ethyl



$$\begin{array}{c} (C_2H_5O_2C)_2{:}C-C{:}(CO_2C_2H_5)_2 \\ \;\;|\quad\;\; | \\ SC-CS \end{array}$$

could be isolated.[2]

This question has now been investigated again, and we give here the results of this investigation. We have examined the action of xanthogenate of potassium on the following halogen derivatives of malonic acid and alkylmalonic acids:

brommalonic acid
isopropyl-brommalonic acid
ethyl-brommalonic acid
benzyl-brommalonic acid.

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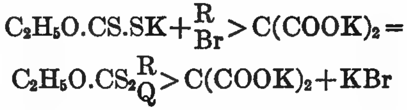
[1] Annalen der Chemie, *339*, 351; *348*, 20 and 133; *364*, 314.

[2] Biilmann: Studier over organiske Svovlforbindelser, Copenhagen 1904 p. 98.

It was found that these acids form xanthogenic derivatives of the malonic acids, the reaction being expressed by the equation

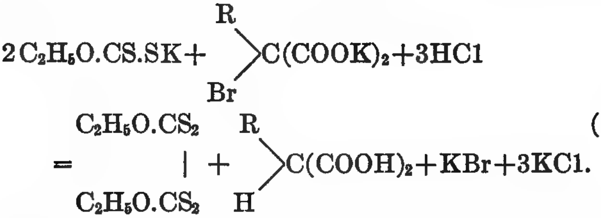


$$C_2H_5O.CS.SK+\genfrac{}{}{0pt}{}{R}{Br}{>}C(COOK)_2=$$
$$C_2H_5O.CS_2\genfrac{}{}{0pt}{}{R}{Q}{>}C(COOK)_2+KBr \qquad (I)$$

It seems that the velocities of these reactions decrease in the order in which the acids are named above. In 24 hours 78, 2–99, 8 per cent had reacted in the said manner.

The xanthogen-malonic acids, which are formed, are very unstable. When the solutions of their alkali salts were acidulated, carbon dioxide was evolved and the xanthogenmalonic acids could not be obtained in a pure state. They were converted into the corresponding monobasic acids, simply by heating the acidulated solutions. In this manner we isolated xanthogenacetic acid and α-xanthogen butyric acid, which have been previously described,[1] and β-phenyl-α-xanthogenpropionic acid, which will be described hereafter.

An entirely different reaction was found to take place, if the mixtures of the solutions of alkali xanthogenate and alkali salts of halogenmalonic acids are acidulated immediately after mixing. Then the halogen is substituted by hydrogen, and the xanthogenate ion is oxydized to "dixanthogen," corresponding to the equation:



$$2\,C_2H_5O.CS.SK+\genfrac{}{}{0pt}{}{R}{Br}{>}C(COOK)_2+3HCl$$
$$=\begin{matrix}C_2H_5O.CS_2\\ |\\ C_2H_5O.CS_2\end{matrix}+\genfrac{}{}{0pt}{}{R}{H}{>}C(COOH)_2+KBr+3KCl. \qquad (II)$$

This change is quantitative, and can be used for the determination of the rapidity with which the process I advances. The dixanthogen can be quantitatively isolated without difficulty, and, being a measure for the part of the halogen compound which at a distinct moment has not yet reacted after process I, it gives, as difference, also the part which has reacted. Besides this reaction, however, a part of the acid is changed by hydrolysis. *E. Hst Madsen*[1] has examined the hydrolysis of these acids and found that when alkali hydroxide is present, the process is monomolecular and consequently a true hydroylsis. Direct determinations, however, of the amounts of xanthogen compounds, which are formed in 24 hours, have shown that under these circumstances, the change I is the main reaction and not the hydrolysis.

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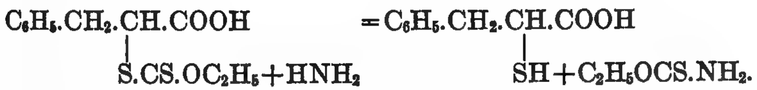
[1] Biilmann, Annalen der Chemie, 1. c.

The β-phenyl-α-xanthogen propionic acid mentioned above was prepared by the action of potassium xanthogenate on the sodium salt of α-bromphenylpropionic acid in aqueous solution at 18°. After 3–4 hours the solution was acidified with hydrochloric acid, and the precipitated acid dissolved in ether. This solution was then dried with sodium sulphate and mixed with pure acetic acid. By the evaporation of the ether, the acid separated in colourless crystals.

The acid melts by 89–90°; it is odourless. In alcohol, ether and hot acetic acid it is very soluble, but slightly in water and cold acetic acid.

The β-phenyl-α-xanthogen-propionic acid was converted into β-phenyl-α-mercaptopropionic acid by treatment with a mixture of aqueous ammonia and alcohol, corresponding to the equation



$$\begin{array}{ll} C_6H_5.CH_2.CH.COOH & = C_6H_5.CH_2.CH.COOH \\ \qquad\qquad\quad | & \qquad\qquad\qquad\quad | \\ \qquad\qquad\quad S.CS.OC_2H_5+HNH_2 & \qquad\qquad\qquad\quad SH+C_2H_5OCS.NH_2. \end{array}$$

The xanthogenamid and the mercapto acid were separated by the method, which has been used with mercapto-acids described in former papers, and the acid was purified by distillation in a vacuum. It boiled at 184–7° under 11–12mm. pressure. 17g. of β-phenyl-α-xanthogenpropionic acid gave 7 g. pure β-phenyl-α-xanthogenpropionic acid, theory 11.5 g.

The new acid is obtained as colourless crystals, which melt at 46°. It has the odour which is characteristic for mercapto acids. In alcohol and ether the acid is very soluble, slightly in water.

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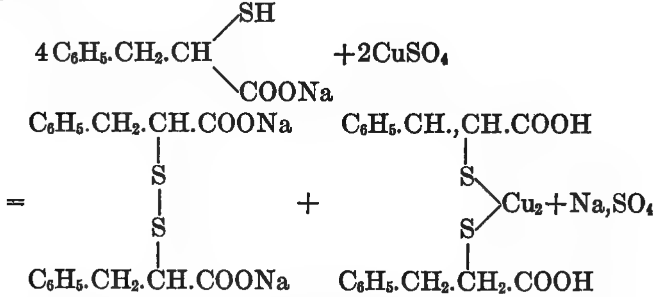
[1] Kritiske Studier over Alkoholaters og Basers Indvirkning paa organiske Halogenforbindelser, Copenhagen 1912.

By the action of copper salts on the alkali salts of the mercapto acid, the latter is oxydized to a disulphide acid, and the cuprous salt of the mercapto acid is precipitated, corresponding the equation:



$$4\,C_6H_5.CH_2.CH\begin{matrix}\diagup SH\\ \diagdown COONa\end{matrix} + 2CuSO_4$$

$$= \begin{matrix}C_6H_5.CH_2.CH.COONa\\ |\\ S\\ |\\ S\\ |\\ C_6H_5.CH_2.CH.COONa\end{matrix} + \begin{matrix}C_6H_5.CH.,CH.COOH\\ |\\ S\diagdown\\ \quad >Cu_2 + Na,SO_4\\ S\diagup\\ |\\ C_6H_5.CH_2.CH_2.COOH\end{matrix}$$

For the preparation of the α-disulphide-β-phenylpropionic acid the mercapto acid is oxydized with iodine, when the disulphide acid was obtained as a crystalline solid.

THE PRODUCTS OF THE LACTIC FERMENTATION OF SUGARS

ALAN A. CLAFLIN
Boston, Mass.

There is a well defined sentiment pervading the literature relating to Lactic Fermentation that the equation $C_6H_{12}O_6 = 2C_3H_6O_3$ does not represent the reaction which actually takes place when a carbo-hydrate solution is fermented by Lactic Bacteria. Indeed Lafar[1] quotes Adolf Mayer as authority for a yield of 83.9 percent Lactic Acid when a solution was fermented presumably by Bacilli Acidi Lactici, and S. Kayser for a yield of 70% when a solution of Lactose is fermented by the same Bacteria. Other observers do not give figures, but the consensus of opinion seems to support the conclusion of Mayer and Kayser that the yield is not over 84 percent Lactic Acid and that considerable quantities of volatile acids are formed. The principal work on Lactic Fermentation has however been done from a bacteriological point of view, and the chemical side is rather nebulous, because when the fermentations are conducted on the small scale that is essential for absolutely pure culture conditions the quantities of acids produced are too minute for accurate analytical determinations. With a method for gravimetric determination of Lactic Acid lacking, and therefore even the determination of the actual Lactic Acid present in commercial samples still a subject of controversy among technical chemists,[2] the doubt about the yield of Lactic acid produced by any particular Bacteria is not surprising.

In this paper it is the purpose to consider the subject only from the chemical side, with no reference to the bacteriological side, to report the observations as made considering the production of Lactic Acid as a factory process.

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[1] Technical Mycology, 1898, vol. 1, p. 226.

[2] Klapproth, Chem. Ztg., 35, p. 1026; and Besson, Ibid., 35, p. 1209–10.

In the first place the statement that the yield of Lactic Acid depends on the nature of the sugar and nutrient material which is current in the literature but based on no particular definitely cited observations, has apparently no foundation in fact. Maltose, hydrolyzed starch and inverted cane sugar give the same results when impregnated with the same Bacteria and given the same treatment. An excess of nitrogenous materials affords attractive opportunity for the development of putrefying bacteria, but this is obviously an abnormal condition, as it is possible to have mashes high in nitrogen produce Lactic Acid with no trace of Butyric Acid (the chemical evidence of putrefactive bacteria) although it is more difficult than with a less fertile mash.

Qualitatively the following volatile acids are found occurring in the Lactic Acid solution, Formic, Acetic, Propionic, Butyric. The separation of these acids from each other and from the Lactic Acid offers difficulties and quantitative results are only approximate. The two dominant acids that may be present are Acetic and Butyric. Formic Acid is apparently never produced in quantity greater than one percent of the original sugar. Propionic Acid occurs in about the ratio of 1 part Propionic Acid to 10 parts Acetic Acid. The percentage of Acetic Acid present depends on the degree of aeration, it may reach the proportion indicated by Kayser of 30 Acetic Acid to 70 Lactic Acid. It is not proven beyond all possibility of question that the same Bacteria produce Acetic Acid in this proportion when abundant air is present and do not produce it at all under anerobic conditions, but bacteriological examination does not disclose any very great difference in the proportion or variety of species present in two ferments which may give widely different ratios of volatile and Lactic Acid. The presence of Butyric Acid is evidence of neglect and is a factor that therefore need not be considered.

Ninety five to ninety seven percent of the sugar may be converted into Lactic Acid, with the formation of not over one-half of one percent of volatile acid. Under conditions which produce this result the balance is unfermented sugar. To ferment out all the sugar involves an increase in the proportion of volatile acids. Thus to ferment all the sugar results in a lower yield of Lactic Acid, e. g. ninety percent Lactic Acid, five percent mixed volatile acids, and the balance unaccounted for probably disappearing as water and carbon-dioxide.

(*Abstract*)

THE PRESENT STATUS OF THE AMERICAN TANNING INDUSTRY

ALAN CLAFLIN
East Boston, Mass.

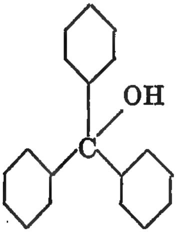
American tanning industry has developed independent of European practice. At present chestnut oak extract constitutes 45% of tannage of sole leather, Quebracho constitutes 25%, Hemlock Bark 15%, Oak Bark 10%, Mangrove, Myrabolams and Valonia 5%. Harness and belt leather tannages about in same proportion as sole leather. Upper leathers are tanned in a constantly increasing proportion by the chrome process. Goatskins are tanned by two bath chrome process. Sheep-skins still tanned largely by vegetable tanning agents. Calf-skins tanned by both one and two bath tannages, when two bath process is used Bi-sulphite of Soda is the reducing agent. Side leather tanned by one bath process. Chrome harness and belt leather not very important. Chrome sole leather growing steadily in importance. Widest use for athletic shoes.

(*Abstract*)

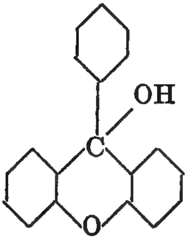
THE SALTS OF ACRIDINE, PYRIDINE AND QUINOLINE

L. H. Cone
Ann Arbor, Mich.

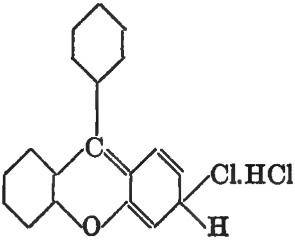
In previous papers it has been shown that the derivatives of the phenyl xanthenols (II) are completely analagous in their reactions to the corresponding derivatives of the triphenylcarbinols (I).



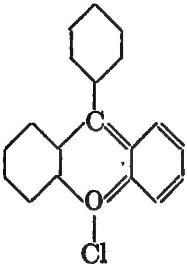
I



II

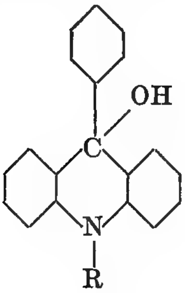


III

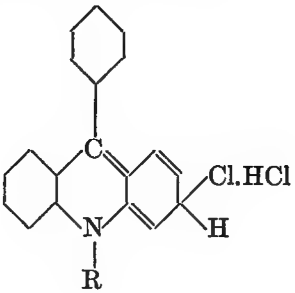


IV

This complete analogy between the oxygen free triphenylcarbinol derivatives and the corresponding derivatives of the xanthenols justified the conclusion that the salts of the latter substances could not be oxonium salts (IV) as had been generally assumed, but must be quinocarbonium salts (III). Experimental results are described in this paper which show that this analogy between the triphenyl carbinols and the xanthenols extends to the derivatives of phenyl acridol (V),



V



VI

and even to the salts of pyridine and quinoline.

The phenylacridols form chloride hydrochlorides VI just as do the xanthenols and the methoxytriphenylcarbinols. From these hydrochlorides normal chlorides have been prepared, which in contrast to the colorless benzoid, normal chlorides of the xanthenols and triphenylcarbinols are quinoid, colored chlorides. These colored acridol chlorides, react however with metallic silver just as does triphenylchlormethane, forming a metal halide and an unsaturated compound analagous to triphenylmethyl. This unsaturated compound is readily oxidizable at the time of its formation and absorbs an amount of oxygen corresponding exactly to the formation of a peroxide of the type of triphenylmethylperoxide. Exactly the same type of reaction takes place between the metals and the salts of pyridine and quinoline but does not take place with open chain ammonium salts. It has also been shown that silver halides form double salts with the salts of the acridols, pyridine and quinoline.

AN IMPROVED METHOD FOR THE PRODUCTION OF MONO-B-AMIDO ANTHRAQUINONE

M. L. Crossley
William Jewett College, Liberty, Mo.

Mono-beta-amido anthraquinone was discovered in 1879 by R. Bourcart and later independently by Hugo von Perger. Both of these men employed the same method for its production and obtained very small yields. They secured the compound by heating anthraquinone mono-beta sodium sulphonate with ammonium hydroxide (25% NH_3) in a sealed glass tube.

Recently I conducted an investigation in which mono-beta amido anthraquinone was the initial compound and in an attempt to follow the directions of Bourcart and Perger for its production, I found that while it was possible to produce the compound by their method, the process was neither safe nor economical. I have experimented with various grades of glass tubes and found in almost every case that the glass will not stand the pressure and dissolving action of ammonia at a temperature high enough to form the mono-beta amido anthraquinone. Of a series of thirty experiments carried out in glass tubes all but two exploded. The yield obtained in the two successful experiments was very small. It was obvious that mono-beta amido anthraquinone could not economically and safely be produced by this method. In addition to the small yield and the uncertainty of success of the experiment the element of danger was too great.

Since the substance was absolutely necessary in my work, and since I had to use it in fairly large quantities, it became evident that a laboratory method for its production would have to be worked out. At the outset it was recognized that any method to be successful as a laboratory process must, as far as possible, minimize the element of danger for the experimenter; must give the largest possible yield and must also be capable of application in a laboratory of moderate equipment. In all about one hundred and ten experiments were carried out. Some of these were successful and others were not, but, as a result of the investigation, the element of danger for the experimenter has been practically eliminated and the yield of the product increased from 14% to 45%.

After considerable experimentation the method which I find best for the production of mono-beta amido anthraquinone is as follows:

Ten grams of anthraquinone mono-beta sodium sulphonate, 124cc ammonium hydroxide (29% NH_3) and 20cc. of water are placed in an extra heavy wrought iron tube, 24″ long and 1″ in dia., one end of which is closed with an inch and one-half threaded plug. The other end of the tube is then closed by a similar plug and the tube shaken several times to facilitate the mixing of its contents. The tube is heated in a bomb-furnace for six hours at 190° C. After the tube cools the plugs are removed and and its contents washed out on a Buchner funnel The amido compound is insoluble in water and must be washed thoroughly with hot water. To purify the mono-beta amido anthraquinone it is recrystallized from ethyl or amyl alcohols. Prepared by this method 4.5 grams are obtained from ten grams of anthraquinone mono-beta sodium sulphonate.

In the production of mono-beta amido anthraquinone a by-product is formed. This is extremely soluble in water and in alkali but insoluble in acid. When the ammoniacal filtrate from the amido compound is treated with hydrochloric acid a brownish flaky precipitate forms. This is very soluble in water and has very high coloring power on animal fibers. This substance is worthy of further investigation.

(*Abstract*)

INTERMEDIATE ADDITION PRODUCTS IN THE REACTIONS OF ORGANIC CHEMISTRY: THE MECHANISM OF THE REACTION IN THE FORMATION OF HYDRAZONES

RICHARD SYDNEY CURTISS AND CHARLES K. HEWES
University of Illinois, Urbana, Ill.

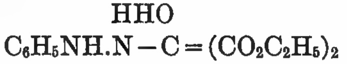
This paper records the results of a study of various hydrazins on methyl oxomalonate. Hydrazons result. The authors believe that substitution according to Dumas' theory rarely occurs in organic reactions. It is believed that molecules first unite. The unstable addition products then separate into ten stable end products of the reaction. They separate such intermediate products and describe them in the case of phenylhydrazin sym. diphenylhydrazin, asym. methylphenylhydrazin, and α Napthylamine, acting on methyl oxomalonate.

(*Abstract*)

THE MECHANISM OF HYDRAZON FORMATION WITH ETHYL OXOMALONATE

Richard Sydney Curtiss and Vanayak Yeshawant Shewade
University of Illinois, Urbana, Ill.

The mechanism of the hydrazon formation with this ketoester is here described.

Phenylhydrazin and ethyl oxomalonate react intensely, forming a hydrazon and water. With great care an intermediate addition product  $C_6H_5NH.\overset{H}{N}-\overset{HO}{C}=(CO_2C_2H_5)_2$ can be separated out. This readily loses the elements of water and gives the hydrazon.

The same intermediate product can be obtained using ethyl dihydroxymalonate $(HO)_2=C=(CO_2C_2H_5)_2$ in place of the ketoester. The reaction is explained, not as a substitution reaction but by a primary dissociation of the dihydroxyester yielding a ketoester, and the latter adding the dissociated phenylhydrazin.

(*Extrait*)

JUSTIN DUPONT ET LOUIS LABAUNE

Argentine, France

Justin Dupont et *Louis Labaune* présentent des observations sur quelques dérivés hydrosulfonés de composés non saturés constituants des huiles essentielles. Ils ont reconnu que les alcools géraniol, linalol, rhodinol, ainsi que le terpinéol, fournissent avec une grande facilité des hydrosulfonates sodiques stables, solubles dans l'eau, par simple agitation à froid avec des solutions diluées de bisulfite de soude exempte de gaz sulfureux. L'alcool cinnamique se comporte de même, mais la proportion d'hydrosulfonate formée est beaucoup moindre. L'éthérification de la fonction alcool leur fait perdre cette propriété additive.

THE CHEMISTRY OF WOOD—THE RESINS OF THE DOUGLAS FIR

George B. Frankforter and Harold H. Brown
University of Minnesota, Minneapolis, Minn.

It is now generally admitted that every important species of the pine family is characterized by its own individual resin or resin acid. Although the prime object in beginning this work was to study the chemistry of the wood itself, the work had not proceeded far when the importance of the resin present led us to change and to give our immediate attention to it. As a result, an acid which has been called betic acid was isolated from the resin which had been extracted from the wood. Recrystallized from 62 per cent alcohol, betic acid appeared as well formed crystals with a melting point of 143.5–144.5°. Analyses gave numbers for the formula $C_{17}H_{24}O_2$. These results were also verified by analyses of its salts and by its neutral equivalent. Molecular weight determinations by the freezing point method, however, gave numbers nearly twice too high for the above formula, doubtless a result of polymerization. In addition to the preparation of the metallic salts, bromine and iodine compounds were made and studied.

Nothing is known concerning the molecular constitution of betic acid at the present time, but it is hoped that work on the various other salts and on the general chemical behavior of the acid itself, may throw some light on the constitutional formula.

(*Abstract*)

CONTRIBUTIONS TO OUR KNOWLEDGE OF THE CONDENSATION REACTION BY MEANS OF ALUMINUM CHLORIDE

PART I.—THE ACTION OF CHLORAL, BROMAL AND ALUMINUM CHLORIDE ON THE PHENOLETHERS

G. B. Frankforter and W. Kritchevsky
University of Minnesota, Minneapolis, Minn.

Aluminum chloride reacts vigorously with the phenolethers in the presence of chloral and bromal at the ordinary temperature, but if the temperature is kept at freezing or even below, the reaction takes place almost quantitatively, forming a series of compounds analogous to those obtained under similar conditions with concentrated sulphuric acid. In all the previous condensation reactions, either sulphuric acid alone was used or with other substances like aluminum chloride. The writers found that anhydrous aluminum chloride reacts with the phenylether in the presence of chloral and bromal quite as readily as sulphuric acid, forming in each the same compounds. Thus substances like dianisyl trichlorethane and diphenytyl trichlorethane may be prepared quite as readily with aluminum chloride as with concentrated sulphuric acid, and in some cases the reaction is more satisfactory than when sulphuric acid alone is used.

CONTRIBUTIONS TO OUR KNOWLEDGE OF THE TERPENES. POLYMERIZATION OF PINENE

G. B. Frankforter and F. W. Poppe
University of Minnesota, Minneapolis, Minn.

It has been shown (Jour. Am. Chem. Soc., 28, p. 1461) that when pinene is treated with nacent chlorine under proper conditions, common pinene hydrochloride is first formed; then follows a series of reactions in which chlorine is substituted for hydrogen in the pinene molecule, resulting in the formation of mono, di, tetra, penta and even nona chlorhydrochlorides. Thus, compounds with ten atoms (73 per cent) of chlorine were prepared by the above described method. It was found that somewhat similar reactions take place when pinene is treated with bromine and iodine, indicating that, under proper conditions, both elements would form analagous derivatives. It required but few experiments to show that bromine, while apparently acting differently from chlorine, readily formed a mono and a dibromide (Wagner and Brickner, Ber. 32, 2302) together with higher brom-compounds. Unless bromine is added cautiously, however, it rapidly decomposes the pinene molecule, making the preparation of the pure poly-derivatives extremely difficult. On this account, iodine was substituted for bromine as it gave more satisfactory results.

Armstrong (Ber. 12, p. 1756), in studying the action of iodine on turpentine, found that by following out experiments similar to those which he and Gaskell (Ber. 11, p. 151) used in studying the action of iodine on camphor, obtained by distilling at 250° C, an oil representing about one half the total weight of the turpentine used. The residue he recognized as colophene but containing a considerable amount of free iodine. It began to decompose at the above temperature, liberating a number of substances, among them ethyl iodide and cymene.

The same year Armstrong and Tilden (Jour. Chem. Soc. 35, p. 733) repeated the work of Rebau obtaining colophene. They were unable, however, to obtain it either from American or French turpentine.

That common resin should be formed from pinene seems in perfect accord with what takes place in nature, as the relationship between pinene and common resin has long since been recognized. As early as 1840, Deville Ann. Chim. Phys. 75, p. 38) succeeded in polymerizing pinene into terebene, a polymer of pinene and an isomer of colophene, Rebau (Compt. rend. 76, p. 1547) in studying the action of concentrated sulphuric acid on turpentine, obtained an oily liquid boiling at 318–320° C. This oil he recognized as identical with that obtained by distilling colophony. It is perhaps identical with the terebene of Deville.

Nothing is known of the constitutional formula of colophene further than the fact that analysis indicate the formula $C_{20}H_{32}$ and that colophene would seem to be closely related to common resin, the principal constituent of which is abietic acid. No attempts seem to have been made to convert colophene to the resin acids.

When iodine is brought in contact with pinene at the ordinary temperature, a violent reaction takes place with a rapid rise in temperature and an evolution of a large amount of hydriodic acid. When equal parts of iodine and pinene are cautiously brought together, the temperature rises from 166° to 180°, or above the boiling point of pinene. If the above quantity of iodine is added all at once, the reaction is extremely energetic, liberating both hydriodic acid and iodine with explosive violence. In case the temperature is allowed to rise, the reaction is complex, resulting in the decomposition of much of the pinene and forming a number of substances, including ethyl iodide and cymene. If the iodine is slowly added and especially if the temperature is kept for several days below 10° C, an entirely different reaction takes place. There are no indications of decomposition and both the hydroiodide and the diiodide are formed.

In the first experiments iodine alone was used and the temperature kept below 10° C. The quantity of iodine which combined with pinene was comparatively small, being less than one third the weight of the pinene used. Even with this quantity of iodine and all the necessary precautions concerning the temperature taken while adding the iodine, a violent decomposition followed an attempt to distil the liquid at ordinary atmospheric pressure.

The first effort to bring about a more complete reaction at the ordinary temperature was made by using aluminum chloride with the iodine. The results were unsatisfactory as some pinene hydrochloride was formed and constantly appeared in fractioning off the iodides. The experiment was therefore repeated, using aluminum iodide instead of the chloride.

To 500 grams of pure pinene, 50 grams of sublimed aluminum iodide were cautiously added. It was necessary to add the iodide in small quantities at a time and to keep the pinene in a freezing mixture on account of the violence of the reaction. After the aluminum iodide had been added and the mixture kept cool for several hours, 600 grams of iodine were then added, a little at a time. After standing for two days in a refrigerator, it was removed, the temperature gradually raised to 100° C and kept at that temperature for several hours. The whole was then transferred to a distilling flask and distilled at a pressure of 5 to 15 millimeters. A preliminary examination of the heavy oily liquid before the distillation, showed that at least three substances were present, an unidentified terpene and two iodine compounds.

The liquid was removed from the aluminum iodide and subjected to distillation in vacuo at 7 mm. pressure. A small amount of liquid passed over at 50° C. This proved to be the terpene mentioned above. The temperature then rapidly rose to 107° C at which point about one-third passed over. The first of this distillate which came over was colored from a small quantity of free iodine. The latter part, however, passed over perfectly clear. It proved to be an iodide of pinene and had a specific gravity of 1.447 and an index of refraction of 1.6245. It decomposed rapidly on standing in sunlight, liberating iodine. Analyses gave numbers for the hydroiodide, notwithstanding the fact that its properties were somewhat different from those given for the simple hydroiodide. (Wagner and Brickner, Ber. 32, 2302). Two analyses gave an average of 48.02 per cent of iodine; theoretical amount is 48.13.

Pinendiiodide, $C_{10}H_{16}I_2$.—After the above iodide had been removed, the distillation was continued, the temperature rising to 125° C. About one-fifth of the total distilled over between 119 and 125° C at 7 mm. Distillation at 7 mm. failed to yield a perfectly colorless oil. At the time of distillation it had a light amber color but turned dark brown from liberation of iodine on standing. The liberation was rapid in sunlight. The oil thus obtained had a specific gravity of 1.69.

Analysis gave the following:

Found: I, 64.85. Calculated for $C_{10}H_{16}I_2$, I 65.12.

Since the diiodide was prepared and analyzed, Cassannova, (Boll. Chim. Farm. 48, 684) obtained by treating pinene with iodine in the presence of almond oil, a diiodide with a yellowish color and a boiling point of 170° C.

Polymerization of Pinene.—As has already been stated, when the iodides of pinene are allowed to stand, especially in sunlight, decomposition begins immediately, liberating free iodine and forming polymers of pinene. Decomposition was observed in the hydroiodide but more especially in the diiodide. In fact, so rapid was the decomposition in the diiodocompound that it could not be obtained without some free iodine, and when finally obtained in a comparatively pure form, it turned black in a very short time when exposed to sunlight, owing to the liberation of iodine. It was found that by either allowing the iodides to stand or by distilling several times, the iodine could be completely removed, leaving behind hydrocarbons entirely free from iodine.

Dipinene, $(C_{10}H_{16})_2$.—Pure pinene was treated with an excess of iodine in the presence of aluminum iodide and allowed to stand for some time in sunlight. It was then subjected to fractional distillation at 7 mm. pressure. At 50° to 55° free iodine passed off and the residue in the flask began to grow clear. The temperature was then raised from 138° to 140°, at which point practically all of the iodine had been removed and the residue changed from a dark brown to a light amber colored liquid. Between 140° and 180° a perfectly clear thick oil, resembling glycerine, distilled over. Most of ti passed over between 160–175. On redistilling, its boiling point ta 7 mm. was 172° and its specific gravity was 0.947 at 20°. Its viscosity at

25° was 101 as compared with water. It is optically inactive but its index of refraction is very high, being 1.52517 at 23°.

It proved to be insoluble in water but soluble in absolute alcohol, ether, chloroform and benzene. It is very stable, resisting nearly all of the common reagents. Fuming nitric acid oxidizes it to an unidentified acid. Three molecular weight determinations by the boiling and freezing point methods gave an average of 282.

Calculated for dipinene $(C_{10}H_{16})_2$ 272.

Analysis gave the following:

C 87.61 and 88.06

H 11.20 and 11.44

Calculated for dipinene $(C_{10}H_{16})_2$ C 88.23 H 11.77

Dipinene resembles colophene very closely and is doubtless an isomer.

Colophonene, $C_{10}H_{16})_4$.—Fractional distillation was now continued, raising the temperature to 230 at 7 mm. pressure. Distillation practically ceased at this point except for a small quantity of a semi-solid substance which collected in the condenser. As soon as the temperature reached 230°, the whole mass in the flask began to fluoresce. After holding the temperature half an hour at 230°, fluorescence became brilliant. Distillation was then stopped, the mass cooled down and examined. The substance proved to be a solid with a melting point of about 100°. It was of a light amber or rosin color, very brittle, breaking with the fracture peculiar to common rosin. In general properties it closely resembled common rosin except that it is insoluble in the alkalies and only moderately soluble in absolute alcohol. By dissolving in absolute and cautiously adding common alcohol, the substance was precipitated as a light yellow crystalline powder, which after repeated recrystallizations, melted at 102°–103°. Like the dipinene, colophene proved to be extremely stable. It is not changed by concentrated mineral acids. Fuming nitric acid after long treatment changes it to an acid which is under investigation at the present time. Two molecular weight determinations gave an average of 539.

Calculated for $(C_{10}H_{16})_4$ 544.

Analysis gave the following: $C=88.01$ $H=11.92$
Calculated for $(C_{10}H_{16})_4$ $C=88.23$ $H=11.77$

The Action of Chlorine on Colophonene.—Free chlorine under ordinary conditions does not attack colophonene but when treated with the nascent element, a chloride of colophonene is formed.

Colophonenetetrachloride, $(C_{10}H_{15}Cl)_4$.—Pure pulverized colophonene was suspended in a solution of potassium permanganate and hydrochloric acid added. After standing for several days, during which time potassium permanganate and hydrochloric acid were repeatedly added with frequent shaking, the insoluble substance formed was filtered off, washed with water and recrystallized several times from alcohol. The substance thus obtained was white, changing to a light yellow on standing in the air. After purifying and drying in a desiccator, the substance was perfectly white. It began to shrink at 115° but finally melted at 119–121°. Two chlorine determinations gave an average of 20.66 Cl.

Calculated for $(C_{10}H_{15}Cl)_4$ $Cl=20.82$

It was also found that sulphuryl chloride would attack colophonene, forming a chlorine compound free from sulphur. The chloride was prepared by dissolving the powdered colophonene in chloroform and treating with an excess of sulphuryl chloride. The solution turned brown immediately and finally black. After standing for some time the excess of the sulphuryl chloride and the chloroform were removed by evaporation, leaving a greenish brown residue with an extremely penetrating odor. This odor was neither due to the chloride itself nor to hydrochloric acid, chlorine, sulphur dioxide or sulphuryl chloride. It resembled phosgen very closely. The slightly waxy substance, remaining after evaporation, was dissolved in absolute alcohol and reprecipitated with common alcohol. It came down as an almost white flocculent powder with indications of crystallization. The substance, repurified by the above method, melted at 99–102°. Two analyses gave an average of 20.81 per cent of chlorine.

Calculated for $(C_{10}H_{15}Cl)_4$ $Cl=20.82$

The two chlorides evidently have the same composition but from the melting points and properties in general, they are probably isomeric compounds. Other derivatives of colophonene are under investigation.

Sufficient data has not been obtained to throw much light upon the molecular constitution of these compounds, but from what work has been done, it seems probable that the pinene rings are doubly joined to each other, in which case the reaction may be represented by the following simple equations:

$$2\,C_{10}H_{16}I_2 = C_{10}H_{16} = C_{10}H_{16} + 2\,I_2 \text{ and}$$
$$4\,C_{10}H_{16}I_2 = C_{10}H_{16} = C_{10}H_{16} = C_{10}H_{16} = C_{10}H_{16} + 4\,I_2.$$

This may be assumed we think from the remarkable stability of the compounds. Work toward the constitutional formula is now in progress.

(Abstract)

ETHERS OR OXIDES IN THE TRIPHENYLMETHANE SERIES

M. Gomberg
University of Michigan, Ann Arbor, Mich.

Ethers or oxides of the triarylmethyls are very near to the hypothetical hexaarylethanes in structure, since in them the two triarylmethyl radicles are separated from each other only by one atom of oxygen. A general reaction is here described by means of which these ethers can be prepared. It is also shown that compounds, supposedly ethers of this type, previously described by others are not in reality ethers. It has been found that these oxides are quite stable, as compared with other classes of bodies also closely related to the hypothetical hexaarylethanes. An explanation is offered in this paper as to why previous attempts to prepare para-hydroxy-triphenylcarbinol chloride have failed. A description of this chloride is given, and on the basis of its general behavior, it is looked upon as a quinocarbonium salt. The existence of this salt in that form furnishes an additional argument in favor of considering the simple colored derivatives, as well as the more complex dyes of the xanthone group, as quinocarbonium, in preference to oxonium, salts.

SUR LA RECHERCHE DE L'IONONE

M. Hanriot
Professen l'Ecole Municipale de Physique et de Chimie,
Paris, France

L'ionone a pris aujourd'hui une grande importance dans la fabrication des parfums où elle tend à remplacer en tout ou en partie l'essence de violettes naturelle. Actuellement il n'existe pas de réaction permettant de la reconnaître chimiquement; on se contente d'utiliser l'évaporation lente du parfum qui permet de saisir son odeur caractéristique, surtout au début de l'évaporation. La réaction suivante permet d'en retrouver moins de un millième.

Lorsque l'on dissout l'ionone dans l'acide chlorhydrique concentré, il se produit une coloration jaune d'or intense; si l'on ajoute de l'hydrate de chloral et que l'on chauffe, la liqueur se colore en violet sale. On laisse refroidir et on agite avec de l'éther. La liqueur se décolore.

La solution éthérée, évaporée à froid sur un verre de montre laisse une véritable matière colorante violette, soluble dans l'eau, instantanément décolorée par l'éther. Cette dernière réaction est si sensible qu'il suffit de verser les vapeurs d'éther sur le verre de montre pour obtenir la décoloration de la matière violette.

L'isoionone donne la même réaction; il est même probable que celle-ci n'a lieu avec l'ionone qu'après sa transformation en isoionone par l'acide chlorhydrique. Il ne m'a en effet pas été possible d'obtenir cette réaction en milieu neutre ou alcalin.

La pseudoionone, ni l'essence d'iris ni l'essence de violettes naturelles ne donnent la réaction qui est encore sensible avec l'ionone à la dose de $\frac{1}{2,000}$. J'ai pu retrouver ainsi des traces d'ionone dans un grand nombre de parfums commerciaux. Enfin la présence des essences naturelles ne paraît pas gêner la réaction.

Je n'ai pas réussi à transformer cette réaction en procédé de dosage de l'ionone ni par voie pondérale, ni par voie colorimétrique. Je n'ai pas davantage pu isoler de composé défini dans cette réaction; j'ai seulement constaté que la matière colorante violette contient du chlore combiné, non enlevable par les alcalis, c'est-à-dire provenant du chloral.

(*Abstract*)

THE KINETICS OF THE INVERSION OF SUCROSE BY INVERTASE

C. S. Hudson
U. S. Department of Agriculture, Washington, D. C.

Measurements by the polariscopic method at 30° of the rate at which the enzym invertase, prepared from bottom, yeast, hydrolyzes pure sucrose in aqueous solution under the conditions of slight acidity which cause the maximum enzymotic activity, show that the reaction deviates from the unimolecular order to a large extent in fourteen per cent sugar solutions, but approaches agreement with this order as the dilution increases. As the concentration of sucrose increases above fourteen per cent the reaction again approaches this order and in fifty and sixty per cent solutions the order is followed within the limits of experimental error.

AN IMPROVED APPARATUS FOR THE DETERMINATION OF CARBOXYL GROUPS IN ORGANIC ACIDS

W. H. Hunter and J. D. Edwards
East Boston, Mass.

Fritz Fuchs[1] has described a very simple and neat method for the determination of carboxyl groups which depends on the fact that even weak organic acids will immediately disengage hydrogen sulphide from solutions of potassium sulphydrate, stable solutions of which may be made by saturating potash solutions with hydrogen sulphide and keeping an excess of this gas in contact with the liquid.

The equation involved is

$$RCOOH+KSH+XH_2S=RCOOK+XH_2S+H_2S$$

one molecule of hydrogen sulphide being evolved for each carboxyl group.

Alcoholic and phenol hydroxyl have no effect, with the following exceptions noted by Fuchs.

I. Halogenized phenols with two hydroxyls, react with one hydroxyl.

II. Phenols with a single nitro group, if para, react.

III. A few phenols with carbonyl present, as methyl phloroglucin, may react.

IV. Lactones ordinarily do not react.

V. Any acid whose potassium salt is not soluble in the hydrosulphide solution, will not react completely.

As the method was first suggested, the hydrogen sulphide evolved was to be determined iodimetrically after absorption in alkali, or the hydrogen evolved by its action on mercury was to be collected. Later the principle of the Victor Meyer vapor density apparatus was used, so that the evolved hydrogen sulphide expelled from an air chamber an equal volume of gas, which was measured in a eudiometer. The present paper is concerned with an improved, accurate apparatus for carrying out the determination in the last manner.

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[1] M. *9*, 1132, 1143, (1888) *11*, 363 (1890).

The old apparatus, as described by Hans Meyer[1], consists of a long-necked flask, with thick walls, an air chamber, with delivery tube, and a device for dropping in the sample. The 10% potassium hydroxide used is freed from carbonate by a slight excess of barium hydroxide solution, and filtered, then saturated with hydrogen sulphide. Some hydrogen sulphide is left in the reaction flask at the beginning of the experiment, and then the stopper bearing the sample in one opening, and connecting with the air chamber, filled with dry air, by a tube in the other opening, is fitted gas tight to the flask. The apparatus is then allowed to stand till it cools after handling, the delivery tube is brought under the eudiometer, and the sample is dropped in by pushing the glass rod through to mark 2. The solution may be used for a second and third determination, by removing the air chamber and refilling it with dry air.

Carried out in this manner, the determination is subject to a large number of errors, some of which may be easily avoided.

The most important source of error is the saturation of the alkali solution with hydrogen sulphide. It is extremely difficult to reach a definite equilibrium point when the gas is simply allowed to bubble through the solution. In the formation of the strongly hydrolyzed sulphydrate, the amount of gas taken up by the solution, and dissolved in the gaseous state, has of course a direct effect on the amount of sulphydrate formed. Now the amount of this dissolved gas obviously depends on the partial pressure of hydrogen sulphide in the gas phase above. For these reasons, special precautions must be taken to eliminate chance in the reaching of a definite equilibrium point in saturating the solution with hydrogen sulphide. For, if the solution is not saturated, the hydrogen sulphide set free in the determination is certain to be partly taken up, and if the solution should chance to be supersaturated by earlier saturation under pressure, the reaching of equilibrium is slow on simple release of pressure, and the evolution of gas by the sample would certainly carry out with it much excess gas.

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[1] Analyse und Konstitutions—ermittelung organischer Verbindungen 2 Auflage, p. 577. See Fig. 1.

Second, there is no way of telling when the large apparatus has reached constant temperature, and a small change in temperature in the large volume of the apparatus produces a change which may make a large error in the relatively small amount of gas evolved.

Third, in the large volume of the apparatus, the back pressure of water in the delivery tube leading to the eudiometer makes a noticeable difference in the volume of gas, as is always found on delivering gas into a eudiometer from a bent delivery tube.

Fourth, convection currents may carry hydrogen sulphide up to the top of the air chamber, if this is not rather long, in which case some will be carried over into the water and lost by solution.

Fifth, the vapor tension of water over 10% hydrosulphide solutions is unknown. The dry air expelled is collected over water, and calculated back to dry hydrogen sulphide, whereas the hydrogen sulphide is really saturated with water vapor at this unknown tension. This causes a positive error of considerable magnitude. For instance, if the vapor tension were as great as that of pure water, at 20° and 760 mm, 2.29 % of the gas passing into the air chamber would be water vapor, leading to a positive error of 2.34%.

The large error just mentioned is opposed by the sixth, a negative error. It is an important yet unavoidable one, due to the partition of the potassium cation between the sulphydrate anion and the anion of the acid introduced. With a solution saturated with hydrogen sulphide, if more undissociated hydrogen sulphide is formed, it can not remain dissolved, but must escape leaving always a definite concentration of hydrogen ion present, due to the dissociation of the hydrogen sulphide. This makes the hydrolysis of the hydrosulphide negligible, but also ensures the partition of the base, as is predicted by the law of concentration effect.

Henderson[1] has already discussed very completely the equilibria between acids and bases in solution, with especial reference to weak acids and bases. It is therefore unnecessary to say more than that if no other errors were present it would be possible to calculate the percent of hydrogen sulphide which should be obtained, or even to read it from the valuable table given by Henderson, provided the concentration of hydrogen ion were known. Since it is not known, it may be well to indicate the order of magnitude of the error, although in the 2N hydrosulphide solution, saturated with hydrogen sulphide, the ratios involved are probably very different from those used in the following calculation: In N/10 solution, the percentage degree of dissociation is given by Walker and Cormack[2] as .075, and for acetic acid by Kohlrausch and Holborn[3] as 1.30. Therefore if acetic acid and hydrogen sulphide were competing for the potassium hydroxide in N/10 solution, the base would be shared in the ratio 1.30: .075, that is, the acetic acid would get but 94.54 percent of the base.

Other errors, of less importance may well occur due to absorption of hydrogen sulphide, to difference in solubility of hydrogen sulphide in the salt solution formed, and to the volume occupied by the sample.

The first four errors mentioned are readily avoided or eliminated by the new apparatus, leaving only the partition effect and the error due to water vapor uncorrected. The apparatus used by the authors (Fig. II) consists of a wide-mouthed reaction-chamber D, about 50 mm internal diameter, and 80 mm from bottom to neck fitted with a rubber stopper bearing three holes. In one hole is placed a sample holder B of the type used on the Victor Meyer vapor, density apparatus. In another there is a delivery tube C for hydrogen sulphide, fitted with a glass stopcock. In the third is inserted a three-way cock A of such a type that either the reaction chamber or the air chamber E, on the other end, may be connected with the atmosphere, while the other is closed, or a direct connection may be made between D and E.

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[1] Am. Soc. *30*, 956 (1908).

[2] J. Soc. *77*, 20 (1900).

[3] Leitvermögen der Elektrolyte.

On the outlet to the air is a narrow rubber tube, which may be closed by a pinch-cock. The air chamber E is about 37 mm in internal diameter, and the open space, between the heavy rubber stoppers is about 360 mm in length. Midway in this space there is placed a loose plug J of glass wool. The rubber stopper in the top of E has two holes, one carrying a glass stop-cock F connecting to the outside air, the other bearing a delivery tube without stop-cock. All glass to rubber joints are made up with a layer of rubber cement, and all the glass tubes are set in with benzene into the rubber stoppers. The trigger of the sample holder is also set in the piece of heavy rubber tubing with benzene. As a result, the apparatus is perfectly gas-tight when properly set up. The only weak point in the apparatus is the rubber connection H between the gas burette and the delivery tube, which becomes porous with repeated stretchings.

The method of using the apparatus is as follows.

PROCEDURE

Test for Tightness of Apparatus

The apparatus is set up just as for use, except that no sample and no solution is present, and the attachment is made to the gas burette. With all outlets closed, the leveling bulb is dropped, and the reading is taken on the burette. The level in a tight apparatus becomes constant almost immediately after the first cooling is compensated for. The effect of a leak in the apparatus is readily distinguished from the effect of a change in temperature. The glass over the air spaces of course must not be touched by the hands at any time. If the apparatus is tight, the burette is detached, and gentle suction is applied at the three-way cock, drawing through the air chamber for at least five minutes, air dried by passing through a calcium chloride tube and a small phosphorous pentoxide tube. Then 25cc of carbonate free potash solution, about 1.5N–2N, is introduced into the reaction chamber by a pipette, through the sample holder. The tube must not be wet, if possible, or the sample may fail to fall readily when released.

Saturation with Hydrogen Sulphide

The following definite conditions have been decided on as the result of experiment. The apparatus is set up in a place sheltered from air currents, with the drying tubes still attached. The three-way cock is turned to connect the reaction chamber with the air, and hydrogen sulphide is allowed to run in till all the air is expelled, to avoid decrease in the partial pressure of the sulphide over the solution. The expulsion of air may, if so desired, be proven by the use of a Schiff nitrometer with KOH, as in a nitrogen determination. A pinch-cock is now fastened on the outlet tube, as the neutral point in this type of cock is not safe, the sample holder is opened to let out air, the sample is introduced, and the stopper replaced. When the gas ceases to bubble into the solution, the reaction chamber is held by the upper edge and shaken well for five minutes. The pinch-cock is now removed from the outlet tube, and the solution shaken three minutes with the gas flowing through. The stream is then slowed down, but allowed to continue till about to drop in the sample, to sweep out any possible remaining excess of gas. As the solution is appreciably warmed by the reaction when the fresh potassium hydroxide solution is first neutralized by hydrogen sulphide it must be allowed to stand for half an hour, with frequent shaking, and a slow current of hydrogen sulphide, before proceeding with the tests. This is obviously only necessary before the first determination.

Test for Constant Temperature in the Air Chamber

The gas burette leveled at about 99 cc is now connected with the air chamber, and leveled again. The heat of the body is sufficient to cause a change here, if care is not taken to avoid getting unnecessarily close to the apparatus. In two minutes, the level of the water in the burette should not change more than 0.1 cc. This is best observed by opening the stop-cock F at the top of the air-chamber at the end of the minutes, when any change in level is at once visible.

Test for Constant Temperature of the Whole Apparatus, and Saturation with Hydrogen Sulphide

When the air chamber is at constant temperature, the hydrogen sulphide is cut off, and connection is made between the reaction chamber and the air chamber. The whole apparatus is thus connected, and all outlets closed. The gas burette is again leveled, and the reaction chamber is held by the top and shaken two minutes. If no change in level greater than 0.1 cc is observed in two minutes, the apparatus is ready. If change occurs, the measured shaking must be repeated. Very rarely at this point two or three successive tests have shown a change in level of 0.2 cc in two minutes. In such cases, no great error is introduced if the determination is at once carried out, and 0.2 cc added to or subtracted from the volume obtained, though of course it is not so accurate as the other procedure. This was done in the last two analyses on tartaric acid. It is probable that the proper correction to apply in such a case would be a little greater than 0.2 cc, but the uncertainty introduced is great enough to make it seem best to use the small correction. It would seem very unwise to apply such a correction if the change in level were greater than 0.2 cc.

The Determination

After a satisfactory final test, the burette reading is taken, and the sample dropped into the reaction chamber. The gas is at once evolved, aided by shaking if necessary. During the evolution, the level in the gas burette must be followed closely by the level in the leveling bulb. When the evolution ceases, the reading is taken rapidly and then the reaction chamber is agitated vigorously for three minutes. The final reading is then taken, and will generally show an increase in volume, though for some reason this does not always occur, practically all the gas being evolved at once by some acids. The temperature and barometer are then observed.

To repeat the determination, it is only necessary to fill the air-chamber again with dry air, and follow the procedure as before from the start of the five minute shaking with hydrogen sulphide under pressure. Fresh solution should be used after the evolution of 100–125 cc of hydrogen sulphide. The results of consecutive experiments should easily check within one percent of error, and under favorable conditions, with practice, much closer work can be done. A sample weighing .1800 g with barometer 760 mm, and $t° = 22.5$, reads directly in percent COOH, on the burette.

The only part of the apparatus which need ever be opened is the reaction chamber D, and that is only necessary to remove the used solution and sample tubes.

The results may be calculated either by the formula given by Hans Meyer[1] giving the weight of replaceable hydrogen:

$$\text{Wt. H} = \frac{V(b-w)000\ 000\ 0\ 5895}{1+00\ 367\ t°}$$

or by the following, giving the weight of carboxyl:

$$\text{Wt. COOH} = \frac{V(b-w)000\ 00\ 2632}{1+.00367\ t°}$$

In these formulae,

V = volume of gas evolved
b = barometric pressure
w = vapor tension of water at t°

The two constants are calculated from the weight of 1 cc of hydrogen, and include the necessary division by 2 for the dibasic hydrogen sulphide, and by 760 for the reduction to normal pressure.

One source of error peculiar to the new method is that if the hydrogen sulphide is impure, as for instance in consequence of being made from ferrous sulphide containing iron, the partial pressure will be less than that of pure hydrogen sulphide, and the solution will contain less until the evolution of fresh pure sulphide in the determination, when a layer of pure hydrogen sulphide covering the liquid, easily may cause a further saturation, this involving a retention of some hydrogen sulphide.

Though this error cannot be large if the hydrogen sulphide is at all pure, it is very easily eliminated entirely by using hydrogen sulphide evolved by the action of dilute sulphuric acid on concentrated sodium sulphydrate solution. The sodium hydroxide solution is well saturated by hydrogen sulphide from an ordinary generator, and then acid is allowed to drop slowly into a funnel immersed in the sulphydrate solution. The end of the funnel tube is best turned up a distance of about an inch from the end, so that after the funnel has been cleared of sulphydrate solution by the descending acid, the evolution of gas becomes regular, and the solution is well stirred.

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[1] loc. cit.

The effect of impure hydrogen sulphide was observed in that it was impossible to check closely work done on different days, until the pure gas was used.

The results obtained by the authors with the new apparatus are given in the following table, together with a set obtained by a student with the new apparatus, by another student with the old apparatus, and by Hans Meyer and Krczmar[1] on cantharic acid using the old apparatus.

TABLE OF RESULTS

New Apparatus

	%COOH	Aver. Found	Av. x 100 Calc.	K x 10^4	No. of det.	Extreme difference
Crotonic	52.33	51.11	97.67	.215[2]	3	.27
Anisic	29.60	28.89	97.60	.32[3]	3	.21
Benzoic	36.89	36.11	97.59	.686[2]	3	.10
Salicylic	32.61	31.92	97.88	10.6[2]	3	.24
Tartaric	60.00	60.47	100.79	9.7[3]	4	.39
Maleic	75.85	76.34	100.64	154.0[2]	3	.42
	Student's Series. First Omitted.					
Anisic	29.60	28.63	96.74		3	.75
	Old Apparatus					
	Student's Series. First Omitted.					
Salicylic	32.61	21.77	66.76		3	2.24
	M. *19*, 715 (1898)					
Cantharic acid	34.18	30.37	88.85		3	3.74

[1] M. *19*, 715 (1898).

[2] White & Jones, Am. *44*, 197 (1910).

[3] Ostwald Z. P. C. *3*, 246 et seq.

The foregoing table shows immediately the efficiency of the apparatus, in comparison with the old one. The precision of the results obtained shows clearly that all the important errors have been eliminated save the two unavoidable ones.

The action of these two is very apparent. It will be noticed that the monobasic acids all give results consistently about 2.4 percent low, increasing a little with the increase in strength to salicylic acid. The two dibasic acids, however, give results about .7 percent high. This is just what is to be predicted from the combined effect of the errors mentioned. The monobasic acids are not a great deal stronger than hydrogen sulphide, though the salicylic acid is much stronger than the others. Therefore the partition effect is rather large, approaching the magnitude calculated for acetic acid in N/10 solution, the affinity constant for acetic acid, $K \times 10^4 = .18$, being of the order of that of the first three acids.

Now the dibasic acid may be viewed as an acid one-half of which is very strong, for one carboxyl is probably practically completely transformed, so to speak, into potassium salt, while the other then dissociates and shares the base with the hydrogen sulphide. One-half of the acid is then practically free from the negative error of partition, and the positive error of the water vapor causes the whole yield to cross the one hundred per cent mark. That this is probably the true explanation is shown by the fact that the tartaric acid is but little weaker than the salicylic, almost equal, in fact, while much weaker than the maleic, yet the yield from the tartaric agrees with the maleic, and not with the salicylic yield, as would be expected if only relative strength of acids were concerned.

It may therefore be expected that monobasic organic acids of ordinary strength will give results from 2 to 2.5 percent low, while dibasic acids will give results about .7 percent high.

EXPERIMENTAL PART

Experiments on Saturation with Hydrogen Sulphide

All the experiments to be described were made with hydrogen sulphide produced by the action of sulphuric acid on concentrated sodium sulphydrate solutions.

On Saturation with Hydrogen Sulphide

The reaction chamber being closed for saturation under pressure, it was found that after no more hydrogen sulphide would bubble into the quiet apparatus, more was readily taken up on shaking the reaction chamber rather vigorously. On shaking for five minutes, it was found that it took a full minute for one more bubble of gas to be delivered, and this was taken as showing that on shaking five minutes the solution had become sufficiently saturated under pressure for our purpose.

On Evolution of Hydrogen Sulphide

At the end of a determination it was found that by vigorously shaking the reaction chamber, more gas could be expelled. Practically all is driven out in two minutes, usually only 0.1–.2 cc being obtained in the third minute. Three minutes was therefore chosen as the time of shaking for expelling excess gas during the saturation, as well as after the determination.

On Constancy of Temperature

The apparatus connected with the gas burette, with all outlets closed, becomes a large air thermometer. In a sheltered part of the room, with reasonably constant temperature, no difficulty is usually experienced in having the temperature so constant that the level will not change more than .1 cc in two minutes, and in many determinations, no change has been observed in that time.

Hydrolysis of the Hydrosulphide

In the sulphydrate solution ready for analysic, phenolphtalein produces no pink color. If a drop or two is allowed to stand in the air a few minutes, phenolphtalein will produce a pink color, after the loss of hydrogen sulphide.

Following are the details of the results obtained with pure hydrogen sulphide, following the procedure exactly as given. The acids were all pure samples, of tested melting point. Stearic acid would not set free any hydrogen sulphide.

Crotonic acid

Calc COOH = 52.33

.1528g gave 44.10 cc at 22° & 744.2 mm = 50.93
.1468g " 42.60 cc " 22° & 744.2 " = 51.20
.1475g " 42.80 cc " 22° & 744.2 " = 51.20
Av = 51.11

$$\text{x } 100\,\frac{\text{Av}}{\text{Calc}} = 97.67$$

Anisic Acid

Calc COOH = 29.60%

.1734g gave 28.5 cc at 21° & 740.2mm = 28.99%
.2103g " 34.4 cc " 21.5° & 740.2mm = 28.78%
.2251g " 37.00 cc " 22.5° & 74.35mm = 28.90%
Av = 28.89

$$100 \text{ x } \frac{\text{Av}}{\text{Calc}} = 97.60$$

Benzoic Acid

Calc COOH = 36.89% $K \times 10^4 = .686$

.1952g gave 40.00 cc at 22° & 740 mm = 35.95%
.2013g " 41.10 cc " 21° & 740.2mm = 36.01%
.1499g " 30.64 cc " 21° & 740.2mm = 36.05%
Av = 36.00

$$100 \text{ x } \frac{\text{Av}}{\text{Calc}} = 97.59$$

Salicylic Acid

Calc COOH = 32.61% $K \times 10^4 = 10.6$

.1858g gave 33.5 cc at 21.5° & 743.1mm = 31.85%
.1798g " 32.65 cc " 21.5° & 743.1mm = 32.07%
.1809g " 32.60 cc " 21.5° & 743.1mm = 31.83%
Av = 31.92

$$100 \text{ x } \frac{\text{Av}}{\text{Calc}} = 97.88$$

Tartaric Acid
Calc COOH = 60.00
.1858g gave 65.56 cc at 22.5° & 727.5mm = 60.67%
.1508g “ 53.20 cc “ 23.5° & 727.2mm = 60.28%
.1492g “ 50.60 cc “ 20.5° & 744.0mm = 60.53%
.1361g “ 46.70 cc “ 20.5° & 742.9mm = 60.65%
Av = 60.47

$$100 \times \frac{\text{Av}}{\text{Calc}} = 100.79$$

Maleic Acid
Calc COOH = 75.85
.1214g gave 52.7 cc at 23° & 743.5mm = 76.14%
.1182g “ 51.6 cc “ 23° & 743.5mm = 76.56%
.1436g “ 62.52 cc “ 23° & 743.2mm = 76.33%
Av = 76.34

$$100 \times \frac{\text{Av}}{\text{Calc}} = 100.6$$

STUDENT'S SERIES

These determinations were carried out by a student absolutely unfamiliar with the method. The first four determinations made are given, and the first determination is excluded from the average, as a practice determination.

Anisic Acid
Calc COOH = 29.60%
.1819g gave 28.0 cc at 20° & 747 mm = 27.54%
.1766g “ 27.9 cc “ 20° & 747 mm = 28.26%
.1714g “ 27.8 cc “ 20° & 747 mm = 29.01%
.2064g “ 32.7 cc “ 19° & 750.5mm = 28.62%
Av = 28.63

$$100 \times \frac{\text{Av}}{\text{Calc}} = 96.74$$

For comparison may be taken two sets obtained with the old apparatus.

I. Salicylic Acid. (By a student unacquainted with the method)

Calculated COOH = 32.61

Found 21.74, 20.66, 22.90

Av = 21.77

$$100 \text{ x } \frac{\text{Av}}{\text{Calc}} = 66.76$$

II. Cautharic Acid [1]

Calculated COOH = 34.18

Found 30.26, 32.3, 28.56

Av = 30.37

$$100 \text{ x } \frac{\text{Av}}{\text{Calc}} = 88.85$$

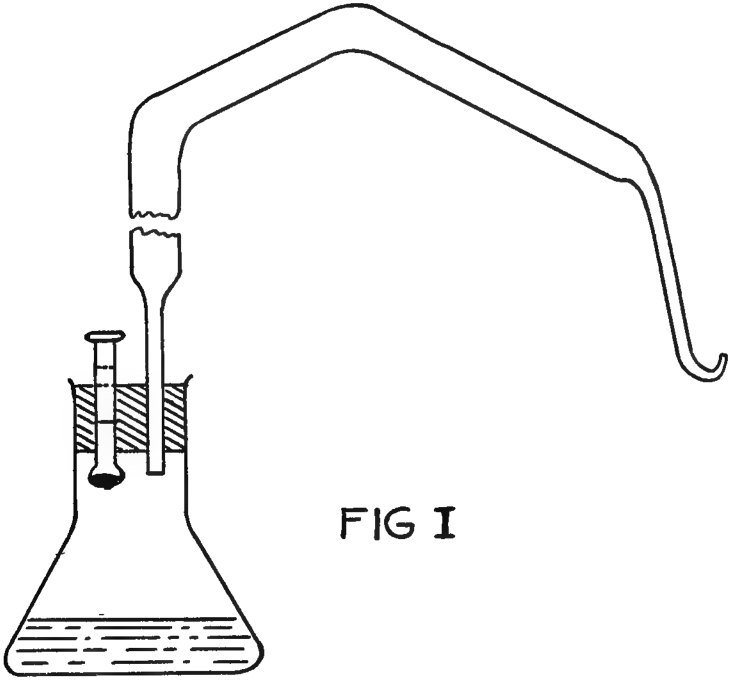
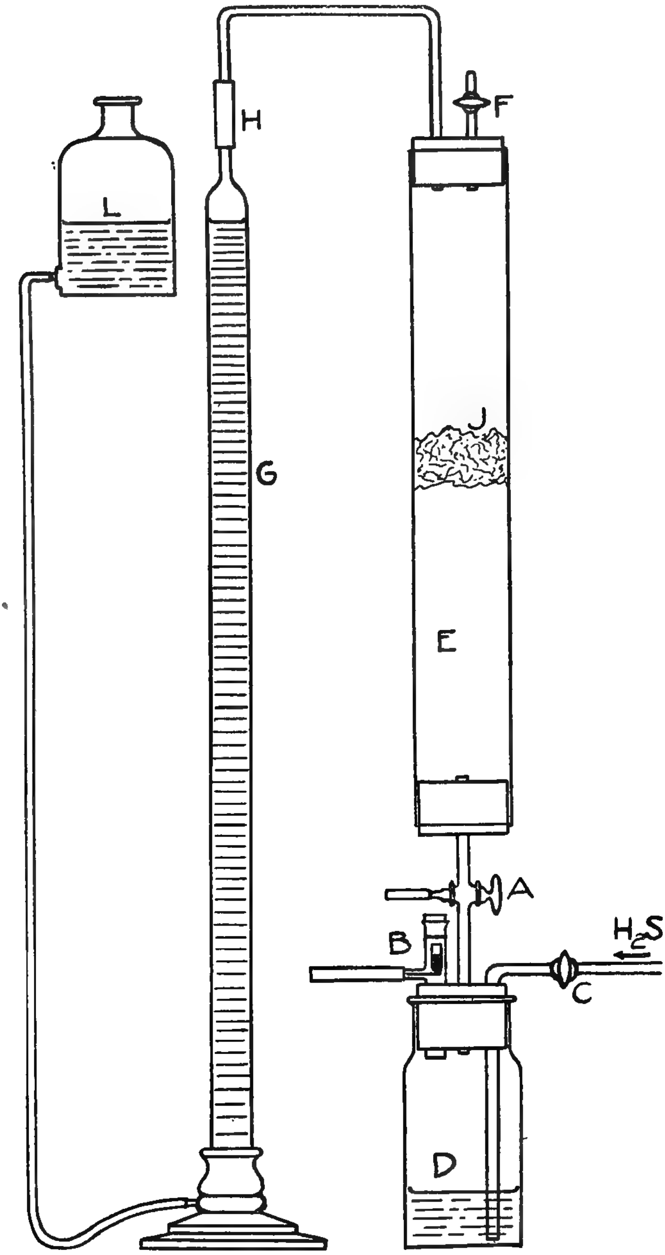


FIG I

[1] M. *19* 715 (1898)


H
F
L
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H_2S
C
D

(*Abstract*)

A CATALYTIC DECOMPOSITION OF SOME PHENOL SILVER SALTS BY ALKYL IODIDES

W. H. Hunter, E. A. Daniels, A. O. Olson and L. Karatz
University of Minnesota, Minneapolis, Minn.

It was found by Torrey and Hunter[1] that undiluted alkyl iodides acting on the dry red or white silver salt of tribromphenol, gave a small amount of tribromphenetol, and a large amount of silver bromide, with a white amorphous compound containing 64% of bromine. The reaction was accompanied by the appearance of a blue color, which then disappeared. Further work by the present authors has shown that this compound has the empirical formula $C_6H_2Br_2O$, which corresponds to a loss of silver bromide from the silver salt of tribromphenol. The substance has, however, a very high molecular weight, and is apparently a polymerization product of the residue left after the splitting out of silver bromide. Like results were obtained with the trichlorphenol and tribromresorc in monomethylether salts.

It was found also that in the last case the same decomposition could be produced by heat alone, or even by standing in dry benzene, giving the same products, and in benzene, with the appearance of the characteristic blue color.

From these facts it is concluded that the reaction is really a decomposition of the unstable silver salt molecule into silver bromide and a residue which polymerized to give the amorphous compound. This decomposition is supposed to be brought about by the catalytic action of heat or the alkyl iodide or benzene. It does not occur if the alkyl iodide is diluted with alcohol or ether. Further work on the reaction, especially with reference to the blue compound, is being carried on.

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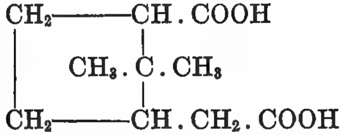
[1] Am. Soc. *33*, 204 (1911).

UBER DIE TOTALSYNTHESE DES FENCHOCAMPHOROUS

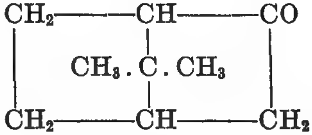
Gust Komppa
Helsinki, Finland

Der Versasser hat aus der früher (Ber. d. deutsch. chem. Ges. 1911) totalsynthetisierten Homoapocamphersaure (=Pinophansaure) Formel I, durch

I.



II.



Trockendestillation ihres Bleisalzes ein Keton (Formel II) erhalten, dessen Semicarbazon bei 220° schmitzt und in allen Beziehungen mit dem Semicarbazon des *rac.* Fenchocamphorous identisch ist. Das letztgenannte wurde aus dem *rac.* Fenchon nach *Wallach* dargestellt.

Hierdurch ist die Totalsynthese des Fenchocamphorous ausgeführt und die Konstitution des letztgenannten Ketons, als ein wirklicher Apocampher nach Formel II, bewiesen.

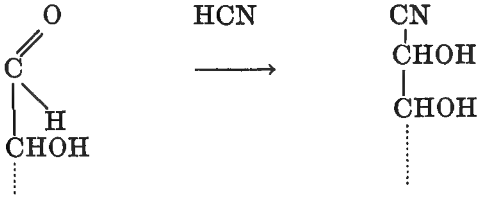
(*Résumé*)

SUR LES CYANHYDRINES DE QUELQUES MONOSACCHARIDES

Cyrill Krauz et Jan Kloud

Laboratoire de chimie organique à l'Ecole polytechnique tchèque de Prague, Bohême

Dans la littérature des hydrates de carbone on représente la réaction des monosaccharides (pentoses et héxoses) avec l'acide cyanhydrique généralement par la formation de deux cyanhydrines suivant le schéma.



Dans certains cas on admet aussi qu'il se forment des amides au lieu des nitriles[1] on n'a toutefois pas réussi jusqu'à présent a les isoler en état pur qui suffirait pour leur caractérisation. La théorie de Le Bel—van't Hoff prévoit lors de l'addition de l'acide cyanhydrique a un sucre réducteur la formation d'un nouveau carbone asymétrique. Par conséquant il doivent se former toujours deux produits d'addition—deux "cyanhydrines" épimères[2] que l'on reconnaît ordinaîrement a leur produits de saponification sans qu'on ait besoin de les isoler avant. Il s'en suit que l'étude de la réaction n'est pas fini par l'isolation de l'un de ces deux isomères et qu'il faut chercher l'autre (plus soluble) dans les eaux-mères.

Dans le cas du mannose[3] on a même fait une supposition invraisemblable que le second isomère fait complètement défaut. Le but de notre travail était d'isoler et de caractériser tous les produit d'addition de l'acide cyanhydrique avec les monosaccharides accessibles. Nous y sommes parvenu dans tous les cas ou nous avons obtenus des produits d'addition solides. Ce qui est intéressant c'est que la réaction nous donnait régulièrement deux amides épimères donc des produits résultants d'une addition de H_2O aux cyanhydrines.

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[1] Kiliani: B. B. *19*, 3022.
Maquenne: C. r. *106*, 286.

[2] Votocek: B. B. 1911, Beitrag zur Nomenklatur der Zuckerarten.

[3] Fischer—Hirschberger B. B. *22*, 365.

1.) ESSAIS AVEC L'ARABINOSE

Nous avons préparé ce sucre en hydrolysant la gomme de cerisier par de l'acide sulfurique de 10% et nous n'avons employé pour nos essais que le produit complètement qui possédait un pouv. rot. de $[\alpha]$ D = +104. 54°.

Lorsqu'on traite la solution d'arabinose avec l'acide cyanhydrique de concentration moyenne, on obtient un mélange cristallisé qui se compose des amides 1-glyconique et 1-mannonique. Nous avons purifié le premier corps en le cristallisant plusiers fois de l'acide acétique glacial; on finit par obtenir une substance cristalline incolore fusible à 181° (Kiliani a trouvé 160°). Pour vérifier qu'il s'agit ici de l'amide 1-glyconique nous avon saponifié notre produit au moyen de la baryte caustique, puis transformé en lactone et réduit par l'amalgame de sodium en glycose lévogyre qui ne nous a donné aucune trace d'hydrazone insoluble dans l'eau. Le deuxième corps—l'amide 1-mannonique, qui reste toujours dans les eaux-mères sous forme d'une substance gommeuse, nous l'avons purifié en la précipitant plusiersfois d'une solution acétique par de l'éther.

Il se sépare dans ces conditions sous forme de substance microcristalline très déliquescente et hygroscopique qui ne possède aucun point de fusion net. L'analyse élémentaire et la transformation de cette substance par saponification et réduction de la lactone en sucre réducteur nous a donné de l'hydrazone de mannose peu soluble dans l'eau. Ceci démontre suffisemment qu'il s'agit ici de l'amide 1-mannonique. Nous avons constaté que—contrairement aux indications des Mr. Fischer et ses collaborateur l'amide solide (p. def. 181°) appartient a l'acide glyconique, tandisque celle des eaux-mères (déliquescente) est un dérivé de l'acide mannonique.

2.) ESSAIS AVEC LE XYLOSE

Nous avons préparé le xylose en hydrolysant la paille de froment. L'addition d'acide cyanhydrique ne nous a fourni que des produit liquides, pour la séparation desquelles nous n'avons pu jusqu'ici trouver de méthode convenable.

3.) CECI S'APPLIQUE ÉGALEMENT AU RHAMNOSE

4.) ESSAIS AVEC LE RHODÉOSE

Pour ce qui concerne la réaction de ce sucre avec l'acide cyanhydrique nous renvoyons le lecteur au travail de l'un de nous, publié dans le Bull. de l'Academie François Joseph de Sciences de Bohême 18^{me} année No. 46. et à la publication dans les B. B. D. deutsch. chem. Ges. *43*, p. 482. On y montre, qu'il se forment deux amides épimères, celle de l'acide α- et celle de l'acide β-rhodéohéxonique.

5.) ESSAIS AVEC LE FUCOSE

Le fucose a été préparé en hydrolysant le *fucus vesiculosus* au moyen de l'acide sulfurique de 10 p. 100. Suivant les indications de Mrs. Mayer et Tollens[1] nous avons additionné le sucre d'acide cyanhydrique et obtenu de cette manière un mélange cristallisé, composé de deux amides solides; l'un d'elle, l'amide—α-fucohéxonique, cristallisé de l'acide acétique glacial, possèdait un p. de f. constant de 200° et fournissait par la saponification au moyen de la baryte caustique un fucohéxonate lévogyre $[\alpha]D = -6.69°$.] L'autre corps qui correspond à l'acide β-fucohéxonique (jusqu'ici non décrit) a été isolé des eaux-mères sous forme d'une poudre microcristalline, fusible (après un traitement a l'alcool méthylique) à 176°. En le saponifiant avec de l'hydrate de barium nous avons obtenu un β-fucohéxonate de barium déxtrogyre: $[\alpha]$ D $= +1.93°$. La concordance des valeurs numériques pour le pouv. rot. était a prévoir, puisque les sucre fucose et rhodéose constituent des antipodes; la différence des points de fusion des amides décrites s'explique facilement si l'on tient compte de ce que l'on n'a pu séparer les deux amides rhodéohéxonique que par lévigation.

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[1] B. B. *1907*, 2434.

6.) *Les dérivés d'addition du glycose* n'ont pu être isolés non plus en état solide, ce qui nous a rendu impossible de les séparer l'un de l'autre.

7.) ESSAIS AVEX LE GALACTOSE[1]

En hydrolysant le lactose on a obtenu après plusieures de cristallisation le galoctase pur qui possèdait un $[\alpha]$ D $= +80.72°$. Par l'action de l'acide cyanhydrique sur le galactose il résultent égallement deux amides, dont l'une, l'amide α-galactohéptonique est bien cristallisable de l'alcool de 60 p. 100. et fond a 201°. En saponifiant cette amide on obtient de l'acide α-galactohéptonique bien caractérisé par sa phénylhydrazide très difficillement soluble dans l'eau et fondante a 226°. Les eaux-mères après la séparation de l'amide α-constituent d'après l'analyse élémentare et la réaction avec la phénylhydrazine un mélange des deux amides, car elles nous ont fournis deux hydrazides, dont l'un fond à 226°, l'autre a 186.°

8.) ESSAIS AVEC LE MANNOSE

Nous nous sommes servi du sucre préparé par l'hydrolyse de l'invoire végétal (phytelephas macrocarpa) sous forme d'un sirop brunâtre, cristallisant bien après amorçage.

Dans les travaux des Mrs. *Fischer et Hirschberger et Hartmann* on trouve[2] l'opinion qu'il ne se forme avec le mannose qu'on seul produit d'addition. Par contre nous avons pu constater, qu'ici encore prennent naissance les deux amides prévues. L'une d'elle se dépose sous forme d'un corps solide microcristallin, fondant après plusieures cristallisations de l'alcool de 60 p. 100 a 214°–215° (Fisher et Hirschberger indiquent 82°–183°). Nous avons caractérisé ce corps après saponification d'une part parl le sel plombique de l'acide correspondant et d'autre, par sa phénylhydrazide difficillement soluble dans l'eau, fusible a 226°. Les eaux-mères après la séparation de l'amide ∝ -sont un mélange des amides ∝ - et β-mannohéptoniques. Le dérivé β nous l'a vous indentifié en saponifiant et le transformant en sel plombique, qui se distingue du sel ∝ -monnohéptonique par sa grande solubilité dans l'eau même à froid. A côté de cela nous avons préparé l'acide β-mannohéptonique libre en traitant son sel plombique par de l'hydrogène sulfuré.

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[1] Maquenne: C. r. *106*, 286.
Kilini: B. B. *21*, 915.
Fischer: A. *288*, 139.
Fischer et Morel: B. B. *27*, 382.

[2] Fischer et Hirschberger: B. B. *22*, 365.
Hartmann: A. 272, 190.

Nous avons transformé cet acide par l'action de la phénylhydrazine en phénylhydrazide.

En comparant ce corps à celui qui résulte lors de l'action de la phénylhydrazine sur l'acide ∝ -mannohéptonique nous avons constaté qu'il s'agit ici d'un dérivé β-mannohéptonique qui ne possède aucun p. de f. constant et se sépare sous forme d'une substance molle, mais cristalline et très soluble dans l'eau même à froid.

Pour plus de sûreté nous avons isomérisé l'acide ∝ -mannohéptonique pur en le chauffant sous pression avec de la pyridine. En traitant le produit obtenu par de la phénylhydrazine nous avons réussi a isoler une hydrazide complètement identique a celle de l'acide β-mannohéptonique déjà décrit.

DIE ZUSAMMENSETZUNG DER HOCHSIEDENDEN MINERALÖLE

(Mitteilung aus dem Kgl. Materialprüfungsamt)

Von Professor Dr. J. Marcusson
Berlin-Lichterfelde W. Germany

Die Bewertung der hochsiedenden Mineralöle (Mineralschmieröle) erfolgt zur Zeit hauptsächlich nach physikalischen Untersuchungsverfahren wie Bestimmung des Flüssigkeitsgrades, der Entflammbarkeit und des Kältepunktes. Diese Prüfungen gestatten aber nur eine begrenzte Kennzeichnung. Genaue Festlegung der Eigenart eines Oeles und Beurteilung seiner Verwendbarkeit ist nur bei gleichzeitiger Berücksichtigung des sehr mannigfachen chemischen Aufbaues möglich.

Die Mängel der bisherigen Prüfungsweise haben sich besonders fühlbar gemacht, seitdem bei der Ringschmierung und im Dampfturbinenbetriebe infolge längerer Verwendung der nämlichen Schmierölmenge erhöhte Ansprüche an die Leistungsfähigkeit und Beständigkeit der Oele gestellt werden. Es hat sich gezeigt, dass Oele von nahezu gleichen physikalischen Eigenschaften im Betriebe ganz ungleichartiges Verhalten zeigen können. Während das eine Oel sich gut bewährt, gibt das andere infolge Verharzung zu unangenehmen Betriebsstörungen Anlass.

Das Endziel Mineralölanalyse muss daher dahin gerichtet sein, eine möglichst scharfe Kennzeichnung der in den Schmierölen enthaltenen Kohlenwasserstoffgruppen neben der physikalischen Prüfung zu erreichen. In diesem Sinne sind die nachfolgenden Untersuchungen ausgeführt.

Bestandteile der Mineralschmieröle

Alle hellen Mineralschmieröle enthalten einerseits gegen chemische Agentien beständige, gesättigte, andererseits von Chemikalien leicht angreifbare ungesättigte Kohlenwasserstoffe. Sowohl die ersteren wie auch die letzteren können ihrerseits wiederum verschiedenen Kohlenwasserstoffreihen angehören. In Frage kommen von schwer angreifbaren Kohlenwasserstoffen insbesondere die Reihe der Grenzkohlenwasserstoffe oder Paraffine, der Naphthene und Polynaphthene, von leichter angreifbaren Kohlenwasserstoffen die Reihe der Olefine, der aromatischen Kohlenwasserstoffe, der Terpene und Polyterpene, sowie die ungesättigten alicyclischen Verbindungen vom Typus des Tetrahydrobenzols, Dihydropentamethylens usw. Ausserdem enthalten die meisten Mineralschmieröle noch geringe Mengen von schwefel—und sauerstoffhaltigen Körpern. Die Gruppierung der wichtigsten Bestandteile der Mineralschmieröle dürfte etwa der folgenden Uebersicht entsprechen:

I. Ungesättigte Kohlenwasserstoffe:
  a)cyclische
    1) aromatische (Benzol-Naphtalinkohlenwasserstoffe usw.),
    2) alicyclische (Terpene, Polyterpene, Dihydro-Tetrahydroverbindungen),
  b) aliphatische (Olefine, Polyolefine).
II. Gesättigte Kohlenwasserstoffe
  a) cyclische (Naphthene, Polynaphthene, kondensierte Naphthene),
  b) aliphatische (Paraffine).

I. DIE CYCLISCHEN UNGESÄTTIGTEN VERBINDUNGEN

(*Aromatische und alicyclische Kohlenwasserstoffe.*)

Zur Bestimmung der Menge der cyclischen ungesättigten Kohlenwasserstoffe wurde die von Nastjukoff 1904 aufgefundene bisher zur Kennzeichnung der Mineralschmieröle noch wenig verwendete Formolitreaktion verwendet.

Mit Formaldehyd und Schwefelsäure bilden die genannten Kohlenwasserstoffe schwer lösliche feste "Formolite," während Paraffine, Naphthene, Polynaphthene und Olefine keine Niederschläge geben.

Die Formolitreaktion ist hier nach zwei Richtungen weiter aus-gebildet worden; einerseits ist die Arbeitsweise vervollkommnet, andererseits ist neben der Bestimmung der Menge auch die Ermittlung der Art sowohl der formolitbildenden wie auch der nicht in Reaktion tretenden Oelanteile ermöglicht worden.

a) *Ausführung der Formolitreaktion*

Es hat sich als zweckmässig erwiesen, die Oele nicht entsprechend der Nastjukoff'schen Vorschrift unmittelbar, sondern erst nach vorherigem Lösen in Benzin mit Formaldehyd und Schwefelsäure zu behandeln, weil andernfalls die Reaktion, insbesondere bei zähflüssigen Oelen, bisweilen sehr unvollständig verläuft. Wiederholt ist hier beobachtet worden, dass die nach Abtrennung des Formolitniederschlages wiedergewonnenen Oelanteile erneut mit Formaldehyd zu reagieren vermögen. Dieser Ueberstand wird bei Verwendung einer Oelbenzinlösung vermieden, weil die Oele in sehr feiner Verteilung der Einwirkung der Reagentien ausgesetzt werden. Das zu verwendende Benzin darf an sich natürlich keine Formolit bildenden Bestandteile enthalten. Bewährt hat sich das vom Amt eingeführte Normalbenzin. Die Versuchsausführung bei der Formolitprobe ist hiernach folgende:

27 g Oel werden in einem Erlenmeyerkolben von etwa 300 ccm. Inhalt in 50 ccm. Normalbenzin gelöst und in dieser Lösung, unter Vermeidung des Schüttelns, mit 30 cm. konz. Schwefelsäure versetzt. Zu dem Gemisch lässt man dann unter Kühlung mit Eiswasser 15 ccm. 40%-ige Formaldehydlösung hinzufliessen und schüttelt nun, unter zeitweisem Belassen in der Kühlflüssigkeit, solange um, bis keine Erwärmung mehr eintritt. Das Reaktionsprodukt lässt man noch eine halbe Stunde bei Zimmerwärme stehen und führt es dann in einen zweiten 1 l fassenden, mit 200 ccm. Eiswasser beschickten Kolben unter Nachspülen mit Wasser über. Die saure Flüssigkeit wird nun mit Ammoniak übersättigt, und der entstehende Niederschlag auf einer weiten Nutsche zunächst mit Benzin zur Entfernung des im Niederschlage befindlichen Oeles, hierauf erst mit Wasser behufs Entfernung des Ammoniaks ausgewaschen. Der Niederschlag wird schliesslich bei 105° bis zum bleibenden Gewicht getrocknet und gewogen.

b) *Menge und Art der formolitbildenden Bestandteile*

Zur Bestimmung der Menge der formolitbildenden Bestandteile wird nach Nastjukoff die Formolitzahl (Menge der aus 100 ccm. Oel erhältlichen Formolite) mit 4 multipliziert. Ueber die Art der in Reaktion tretenden Anteile war bisher näheres nicht bekannt. Gemäss nachfolgendem kann man in einfacher Weise sowohl die Menge wie auch die Art der fraglichen Anteile ermitteln, wenn man die bei Ausführung der Formolitreaktion erhältliche Benzinlösung weiter verarbeitet.

Diese Lösung enthält die nicht mit Formaldehyd und Schwefelsäure reagierenden Olefine, Naphthene, Polynaphthene und Paraffine.

Zieht man die beim Abdestillieren des Benzins verbleibenden Oelanteile von der Menge des zur Prüfung verwendeten Oeles ab, so erhält man aus der Differenz die Menge der cyclischen ungesättigten Kohlenwasserstoffe.

Bestimmt man Flüssigkeitsgrad, spezifisches Gewicht, Brechungszahl usw. der wiedergewonnenen Oele und der ursprünglichen, so lassen sich, bei gleichzeitiger Zugrundelegung der Mengenverhältnisse, die entsprechenden Eigenschaften der cyclischen ungesättigten Kohlenwasserstoffe berechnen.

In der beschriebenen Weise sind die Hauptbestandteile von vier russischen und drei amerikanischen Mineralmaschinenölen nach Menge und Art gekennzeichnet worden. (vergl. Tab. 1 und 2).

Aus der Tabelle 1 geht hervor, dass die untersuchten amerikanischen Oele höhere Formolitausbeuten als die russischen ergeben. Der Prozentgehalt an Formolit betrug bei ersteren Oelen 30–33%, bei letzteren 10–24%. Die Formolitmenge steigt im allgemeinen mit zunehmendem Flüssigkeitsgrade. Dass Oel Nr. 3 etwas mehr Formolit ergeben hat als das zähflüssigere Oel Nr. 2, dürfte darauf zurückzuführen sein, dass Probe 3 im Gegensatze zu den übrigen untersuchten Proben unraffiniert war. In ungereinigten Oelen sind naturgemäss grössere Mengen unbeständiger Verbindungen enthalten als in gereinigten. Je grösser der Formolitniederschlag gefunden wird, desto geringer ist die Menge der wiedergewonnenen Oele, deren Prozentgehalt in der vierten Spalte der Tabelle aufgeführt ist.

Tabelle 1

Verhalten amerikanischer und russischer Öle bei der Formolitreaktion.

I.	II.	III	IV	V		VI		VII	
Lfd. №	Art des Öles	Formolitniederschlag	Wiedergewonnenes Öl	Spezifisches Gewicht bei 15 C° × 10000		Brechungsexponent bei 15 C°		Flüssigkeitsgrad nach Engler bei 20 C°	
		%	%	des ursprünglichen Öles	des wiedergewonnenen Öles	des ursprünglichen Öles	des wiedergewonnenen Öles	des ursprünglichen Öles	des wiedergewonnenen Öles
1 raff.	Amerikanische Öle	28.9	74,3	8910	88,56	1,4962	1,4883	11,0	14,9
2 raff.		etwa 30	75,2	9207	9064	1,5168	1,5022.	24,4	28,4
3 unraff.		33,3	74,8	8994	8842	1,5032	1,4882	12,1	12,9
4 raff.	Russische Öle	10,4	88,1	9011	8986	1,4950	1,4912	14,5	24,8
5 raff.		17,1	—	9090	9061	1,5002	1,4962	42,5	64,2
6 raff.		17,8	88,9	9122	9051	—	—	47,4	52,9
7 raff.		24,1	78,7	9108	9070	1,5015	1,4988	62,0	70,8

Tabelle 2

Menge und Eigenschaften der cyclischen ungesättigten Kohlenwasserstoffe amerikanischer und russischer Öle.

Lfd. Nr.	Art des Öles	Kohlenwasserstoffe		Spez. Gewicht bei 15 C° ×10000			Brechungszahl bei 15 C°			Flüssigkeitsgrad bei 20 C°		
		cyklische ungesättigte %	sonstige %	des ursprünglichen Öls	der cyklischen ungesättigten Kohlenwasserstoffe	der fertigen Kohlenwasserstoffe	des ursprünglichen Öls	der cyklischen ungesättigten Kohlenwasserstoffe	der fertigen Kohlenwasserstoffe	des ursprünglichen Öls	der cyklischen ungesättigten Kohlenwasserstoffe	der fertigen Kohlenwasserstoffe
1 raff.	Amerikanische Öle	25,7	74,3	8910	9069	8856	1,4962	1,5191	1,4883	11,0	4,2	14,9
2 raff.		24,8	75,2	9207	9680	9064	1,5168	1,5609	1,5022	24,4	9,1	28,4
3 unraff.		25,2	74,8	8994	9479	8842	1,5032	1,5476	1,4882	12,1	5,3	12,9
4 raff.	Russische Öle	11,9	88,1	9011	9196	8986	1,4950	1,5227	1,4912	14,1	—	21,8
6 raff.		11,1	88,9	9122	9736	9051	—	—	—	47,4	8,0	52,9
7 raff.		21,3	78,7	9108	9250	9070	1,5015	1,5193	1,4968	62,0	23,3	79,8

Vergleicht man die physikalischen Eigenschaften der ursprünglichen und der wiedergewonnenen Oele (Spalte V–VII der Tabelle 1), so ergibt sich zunächst, dass die wiedergewonnenen Oele stets geringere Werte für spezifisches Gewicht und Brechungszahl ergeben als die ursprünglichen. Die in Form unlöslicher Formolite herausgeschafften ungesättigten cyclischen Kohlenwasserstoffe müssen demnach höheres spezifisches Gewicht und höhere Brechungszahlen haben als die ursprünglichen Oele. Dieser Befund steht im Einklang mit der Tatsache, dass einfach zusammengesetzte aromatische Kohlenwasserstoffe wie Benzol, Toluol und die Homologen, welche mit Formaldehyd reagieren, stets ein höheres spezifisches Gewicht und stärkeres Lichtbrechungsvermögen zeigen als die gleich kohlenstoffreichen (mit Formaldehyd nicht reagierenden) Kohlenwasserstoffe der Naphthen—oder Paraffinreihe. Aus Spalte VII der Tabelle 1 geht ferner hervor, dass der Flüssigkeitsgrad der wiedergewonnenen Oele betrachtlich grösser ist als derjenige der ursprünglichen. Dieser Befund lässt in Verbindung mit der quantitativen Bestimmung der formolitbildenden Anteile den Schluss zu, dass Hauptträger der Schmierfähigkeit von Mineralmaschinenölen die mit Formaldehyd und Schwefelsäure nicht reagierenden aus Olefinen, Paraffinen, Naphthenen und kondensierten Naphthenen bestehenden Anteile sind.

In Tabelle 2 sind die (berechneten) Eigenschaften der cyclischen ungesättigten Kohlenwasserstoffe zusammengestellt.

II. UNGESÄTTIGTE ALICYCLISCHE KOHLENWASSERSTOFFE UND OLEFINE

Die Formolitreaktion gestattet zwar, wie oben angegeben ist, die Gesamtmenge der cyklischen ungesättigten Kohlenwasserstoffe und deren physikalische Eigenschaften festzustellen, sie lässt aber keine Schlüsse darüber zu, ob die fraglichen Kohlenwasserstoffe der aromatischen, der alicyklischen Reihe oder beiden Reihen angehören. Die ungesättigten alicyklischen Verbindungen unterscheiden sich von den aromatischen durch das Vorliegen einer oder mehrerer olefinischer Doppelbindungen im Kern und sind daher durch Additionsreaktionen ausgezeichnet. Sie zeigen demnach beträchtliche Jodzahlen. Die Bestimmung der Jodzahl gibt aber, da auch aliphatische Olefine in den Oelen enthalten sein können, nur ein gemeinschaftliches Mass für ungesättigte alicyklische Verbindungen und Olefine. In nachfolgender Tabelle 3 sind die (nach Hübl-Waller bestimmten) Jodzahlen einer grösseren Reihe von Oelen amerikanischen und russischen Ursprungs zusammengestellt. Hiernach schwanken die Jodzahlen von 3, 3–15, 3. Die Jodzahlen der russischen Oele liegen stets niedriger als diejenigen der amerikanischen, sie betrugen im Höchtfalle 5, 6, während die amerikanischer Oele in der Jodzahl meistens über 8 hinaus gingen; nur in einem Falle wurde die niedrige Jodzahl 6, 1 beobachtet. Das Jodaufnahmevermögen steigt bei russischen Oelen im Allgemeinen mit dem Flüssigkeitsgrade. Wenig zähflüssige Oele zeigen sehr geringe nur einige Einheiten betragende Jodzahl.

Nach dem Ergebnis der Jodzahlbestimmung weisen die amerikanischen Mineralschmieröle grösseren Gehalt an Kohlenwasserstoffen mit olefinischer Bindung auf als die russischen. Dieses Ergebnis steht im Einklang mit den von Graefe[1] bei der Untersuchung von Petroleumproben gemachten Beobachtungen.

Dass in den Mineralschmierölen ungesättigte alicyclische Verbindungen, insbesondere Terpenkohlenwasserstoffe vorkommen, hat man schon allgemein angenommen. Ob aber auch aliphatische Olefine zugegen sind, stand, soweit hier bekannt ist, bislang nicht fest. Olefine vermögen bekanntlich nach den grundlegenden Untersuchungen von C. Engler und seinen Mitarbeitern[2] bei längerer Einwirkung von Druck und Wärme, Faktoren, die im Erdinnern immer gegeben waren, unter Ringschluss in Naphtene überzugehen.

Eine Entscheidung in der aufgeworfenen Frage lässt sich nun aber durch geeignete Verbindung der Jodzahlbestimmung mit der Formolitprobe herbeiführen.

Waren in einem Oel nur ungesättigte-alicyclische Verbindungen zugegen, so müssen diese bei der Einwirkung von Formaldehyd und Schwefelsäure in Form unlöslicher Formolite ausgefällt werden, die wieder abscheidbaren nicht in Reaktion getretenen Anteile müssen die Jodzahl 0 aufweisen. Waren dagegen

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[1] Petroleum 1905/906 S. 23. u. 638.

[2] Ber. d. chem. ges. 1909 S. 4610–4631 und 1910 S. 388–411.

Tabelle 30

Jodzahl amerikanischer und russischer Öle in Beziehung zum Flüssigkeitsgrad und spez. Gewicht

Lfde Nr	Art des Öles	Flüssigkeitsgrad nach Engler bei 20 C° (Wasser von 20 C° = 1)	Spez. Gewicht bei 15 C° × 1000 (Wasser von 4 C° = 1)	Jod-Zahl
1	Amerikanische Öle	9,1	8756	11,7
2		11,0	8910	8,2
3		12,1	8994	9,9
4		15,0	8930	9,1
5		20,9	8727	10,4
6		24,4	9207	10,7
7		30,0	9053	6,1
8		31,7	8774	10,4
9		31,9	9060	8,0
10 *)		—	9453	15,3
11 *)		—	9408	15,0
1	Russische Öle	14,1	9011	3,3
2		25,4	9053	3,9
3		42,5	9090	5,0
4		61,9	9108	5,6

*) No 10 und 11 sind Zylinderöle

ausserdem Olefine zugegen, so muss in dem wieder gewonnenen Oel immer noch eine merkliche Jodzahl gefunden werden. Die Versuche haben ergeben, dass in den meisten der untersuchten Oele auf dem angegebenen Wege Olefine nachweisbar waren. Die Jodzahl der Oele wurde durch die Formolitbehandlung zwar verringert, ergab aber in der Mehrzahl der Fälle noch einen merklichen Wert. Im einzelnen sind die Ergebnisse in Tab. 4 zusammengestellt.

TABELLE 4

Jodzahl von Oelen vor und nach der Formaldehydbehandlung

Lfd. Nr.	Art des Oeles	Flüssigkeitsgrad nach Engler bei 20°	Spezifisches Gewicht bei 15°	Jodzahl	
				des ursprünglichen Oeles	des vom Formolitniederschlag abgetrennten Oeles
1	Amerikanische Oele	11,0	8910	8,2	2,6
2		24,4	9207	10,7	3,2
3		12,1	8994	9,9	6,3
4	Russische Oele	14,1	9011	3,3	0
5		42,5	9090	5,0	1,4
6		47,4	9122	1,5	0
7		62,0	9108	5,6	2,5

III Paraffine, Naphtene und Polynaphtene

Während sich nach der Formolitreaktion nur die cyclischen ungesättigten Kohlenwasserstoffe bestimmen lassen, schien Einwirkung starker Salpetersäure geeignet, die gesamten ungesättigten Verbindungen, also ausser den cyclischen Kohlenwasserstoffen auch die aliphatischen Olefine der Menge nach zu ermitteln und von den gesättigten Kohlenwasserstoffen, den Paraffinen, Naphtenen und Polynaphtene zu trennen. Die Bestimmung musste freilich derartig ausgeführt werden, dass eine tiefer greifende, zerstörende Wirkung der Salpetersäure nach Möglichkeit vermieden wurde. Zu diesem Zweck wurden die Oele nicht unmittelbar, sondern in Benzinlösung der Einwirkung der Säure ausgesetzt, die Reaktionstemperatur wurde auf −10° gehalten. Die Versuchsausführung war folgende:

10 ccm. Oel wurden in ebensoviel bis 50° siedendem Benzin[1] gelöst, die Lösung liess man tropfenweise in 30 ccm. rauchende auf −10 abgekühlte Salpetersäure vom spezifischen Gewicht 1,52 im Verlaufe von etwa einer halben Stunde einlaufen. Zur dauernden Erzeugung einer Abkühlung von −10° verwendet man zweckmässig eine 15%-ige Kochsalzlösung, welche ihrerseits durch ein Gemisch von Eis und Salz gekühlt wird. Nach beendetem Einlaufen der Oellösung fügte man zu dem Reaktionsgemisch 50 ccm. gekühlte concentrierte (nicht rauchende) Salpetersäure hinzu und führt dann die gesamte Flüssigkeit in einen Scheidetrichter über. Man bemerkt dann stets 3 Schichten, eine untere wässrige, welche die gesamte Salpetersäure und die löslichen Reaktionsprodukte enthält, eine obere hellgelb gefärbte, in der sich in wesentlichen die nicht angegriffenen Oelanteile in Benzinlösung befinden und eine geringe braunschwarze ölige Zwischenschicht, welche anscheinend aus gewissen Umwandlungsprodukten der in den Oelen ursprünglich enthaltenen Olefine besteht.

Die untere Salpetersäure Schicht wird auf Eis gegossen, wobei sich die Umsetzungsprodukte in Form eines hellgelb gefärbten Niederschlags absetzen. Dieser wird auf einer Nutsche abgesaugt, mineralsäurefrei gewaschen und bei Zimmerwärme getrocknet. Man erhält so characteristische Dinitroverbindungen mit 6, 5–F, 5% Strickstoff.

Die Benzinschicht, welche Paraffine, Naphtene und Polynaphtene (condensierte Naphtene) enthält, wird durch Auswaschen zunächst mit Wasser, dann mit stark verdünnter Lauge und schliesslich wieder mit Wasser von der noch anhaftenden Säure befreit, schliesslich wird das Lösungsmittel abdestilliert und der Rückstand gewogen.

[1] Dieses wird von der Salpetersäure kaum angegriffen, Normalbenzin, welches bei der Formolitprobe Anwendung fand, reagiert dagegen mit starker Salpetersäure unter Bildung merklicher Mengen von wasserlöslichen Stoffen (Azelainsäure usw); die höher siedenden Benzine bilden ölige wasserunlösliche zu Aminenreducierbare Nitroverbindungen.

Auf die Untersuchung der Zwischenschicht, welche meistens nur 3–5% beträgt, ist zunächst nicht weiter eingegangen.

Im übrigen sind die Ergebnisse der Salpetersäureprobe in der nachfolgenden Tabelle 5 zusammengestellt.

Vergleichsweise sind daneben die Ergebnisse der Formolitprobe (aus Tab. 1) aufgeführt. Aus der Zusammenstellung geht hervor, dass die untersuchten amerikanischen Oele in jedem Falle grössere Ausbeute an Nietrierungsprodukten ergaben als die russischen, sie enthielten also weniger gegen Salpetersäure beständige gesättigte Kohlenwasserstoffe.

Sehr bezeichnend ist ein Vergleich, der bei der Bestimmung des Flüssigkeitsgrades der Oele vor und nach der Einwirkung von Formaldehyd und Schwefelsäure einerseits, von Salpetersäure andrerseits erhaltenen Werte (Spalte VI der Tabelle 5).

In jedem Falle zeigt das von der Formolitreaktion wiedergewonnene Oel den höchsten Flüssigkeitsgrad, das von der Salpetersäure unangegriffene Oel war fast in allen Fällen an dünnflüssigster, das ursprüngliche Oel nahm eine Zwischenstellung ein. Daraus geht hervor, dass bei der Formolitreaktion nur weniger zähflüssige, im Schmierwert als minderwertig anzusehende Kohlenwasserstoffe herausgeschafft werden, während bei der Salpetersäureprobe auch die wertvollen Bestandteile der Schmieröle angegriffen werden.

Ob letzteres Verhalten nur auf Zerstörung der Olefine zurückzuführen ist oder ob auch Polynaphtene usw. in Mitleidenschaft gezogen werden, soll durch weitere Untersuchungen festgestellt werden.

Dass bei der Salpetersäureprobe ein stärkerer Eingriff als bei der Formolitreaktion erfolgt, geht auch aus den Ergebnissen der Bestimmung des spezifischen Gewichts und des Brechungsexponenten hervor. In jedem Falle wurden nach Einwirkung der Salpetersäure in dem wiedergewonnenen Oel niedrigere Werte erhalten als in dem von der Formolitreaktion herrührenden Oele (Spalte VII u. VIII der Tab. 5).

Im bearbeiten ist noch die Frage der Trennung von Paraffin- und Naphtenkohlenwasserstoffen. Hierüber wird später berichtet werden.

Tabelle 5

Übersicht über das Verhalten amerikanischer und russischer Öle bei der Formolitreaktion und Sulfurierungsprobe.

I	II	III	IV	V		VI			VII			VIII		
				Rückgewonnenes Öl %		Flüssigkeitsgrad bei 20°C			Spez. Gewicht bei 15°C ·10000			Brechungsexponent bei 15°C		
							des wiedergewonnenen Öls			des wiedergewonnenen Öls			des wiedergewonnenen Öls	
Lfd. Nr.	Art des Öls	Formolitniederschlag %	Nitroverbindungen*) %	aus der Formolitprobe	aus der Sulfurierungsprobe	des ursprünglichen Öls	aus der Formolitprobe	aus der Sulfurierungsprobe	des ursprünglichen Öls	aus der Formolitprobe	aus der Sulfurierungsprobe	des ursprünglichen Öls	aus der Formolitprobe	aus der Sulfurierungsprobe
1 raff.	Amerikanische Öle	28,9	28,1	74,3	73,0	11,0	14,9	9,0	8910	8856	8807	1,4962	1,4883	1,4753
2 raff.		über 30	45,3	75,2	56,2	24,4	28,4	16,4	9207	9064	9040	1,5161	1,5022	1,4812
3 nicht raff.		33,3	36,7	74,8	64,8	12,1	12,9	—	8994	8842	—	1,5032	1,4882	—
4 raff.	Russische Öle	10,4	25,5	88,1	75,5	14,1	21,8	14,1	9011	8986	8932	1,4950	1,4912	1,4521
5 raff.		17,1	24,2	—	81,4	42,5	64,2	—	9090	9065	—	1,5002	1,4962	1,4891
6 raff.		17,8	23,0	88,9	73,4	47,4	52,9	40,2	9122	9051	9050	—	—	—
7 raff.		24,4	—	71,7	—	62,0	70,8	48,5	9108	9070	9049	1,5015	1,4968	1,4576

*) Zu den festen Nitroverbindungen kommen als Reaktionsprodukte noch 3-5% Ölanteile aus der Zwischenschicht hinzu

NEUE METHODE ZUR IDENTIFIZIRUNG DES METHYLALKOHOLS

Von Dr. P. N. Raikaw
Sofia

Seitdem der rohe Holzgeist als Denaturirungsmittel für den gewöhnlichen Alkohol Verwendung findet, ist die Auffindung von sicheren Methoden zur Identifizirung des Methylalkohols ein wichtiges Problem für den praktischen Chemiker geworden; denn als ein schwierig abtrennbarer Bestandteil des denaturirten Alkohols dient die Konstatirung des Methylalkohols zur Identifizirung eines renaturirten Spiritus. Es sind bis jetzt eine Anzahl von Methoden zur Erkennung des Methylalkohols vorgeschlagen worden. Die überwiegende Zahl derselben beruht auf der Überführung desselben (durch Oseydation) in Formaldehyd oder Methylal und Identifizirung der letzteren auf sehr verschiedene Weisen. Bei anderen Methoden wird der Methylalkohol in bestimmte typische Verbindungen übergeführt, aus deren Zustandekommen man auf die Anwesenheit dieses Alkohols rückschliesst.

In der letzteren Gruppe gehört auch die von mir gefundene Methode. Sie beruht auf der von mir gemachten Beobachtung des ungleichen Verhaltens des Nitrometans und seiner nächsten Homologen gegenüber dem Nitroprussidnatrium in alkalischer ev. ammoniakalischer Lösung. Versetzt man nämlich eine Lösung von Nitromethan mit Ammoniak und dann tropfenweise mit einer wässerigen Lösung von Nitroprussidnatrium, so bildet sich auch bei Spuren von Nitromethan schon durch den ersten Tropfen der Nitroprussidlösung eine intensive Indigblaufärbung, welche durch das weitere Intropfen an Stärke zunimmt. Die blaue Färbung ist ziemlich unbeständig und geht je nach den relativen Mengen des Nitromethans und des Nitroprussidnatriums in kürzerer oder längerer Zeit durch's Grün ins Gelb bezw. ins Gelbrot über. Die indigblaue Färbung tritt nach neuen Zusatz von Nitroprussidlösung wieder auf, falls das Gemisch noch unverbrauchten Nitromethan enthält, sodass man das Auftreten und Verschwinden der blauen Färbung beliebige Male wiederholen kann.

Die dem Nitromethan nächstfolgenden höheren Nitroparaffine (Nitroäthan, Nitropropan etc.) liefern unter denselben Bedingungen nur rein kirschrothe Färbungen, ähnlich derjenigen, welche die alkalische Nitroprussidlösung mit Azeton bildet, aber bedeutend schwächere.

Da die blaue Färbung durch Nitromethan auch durch den ersten Tropfen des Nitroprussids intensiv auftritt, während die rote Färbung durch Nitroäthan erst nach Zusatz von mehreren Tropfen intensiv wird, so erlaubt dieser Umstand auch die kleinste Menge des Nitromethans in Nitroäthan scharf zu konstatiren.

Die angeführten Tatsachen lassen sich zu einer sicheren Identifizirung des renaturirten Spiritus durch seinen Gehalt an Methylalkohol verwenden. Dazu verfährt man auf folgende Weise: Etwa 200 ccm. des zu untersuchenden Alkohols werden mit Phosphorsäure angesäuert und mit Hilfe eines Fraktionirrohres der Destillation unterworfen, wobei man die ersten 10 ccm. des Destillates zur Untersuchung auf Methylalkohol verwendet. Dieses Destillat wird in einem Kölbchen von etwa 60 ccm. Inhalt mit 4 gr. roten Phosphor vermischt und bei aufgesetzten Rückflusskühler allmählich mit etwa 25 gr. Jod versetzt. Nach 20 Minuten wird das Gemisch fraktionirt, und die ersten 5 ccm. des Destillates werden in einem kleinen Kölbchen mit 2–3 gr. Silbernitrit einer langsamen trockenen Destillation unterworfen. Das übergehende Destillat wird in einzelnen Eprouvettchen zu je 3–4 Tropfen aufgefangen und auf Nitromethan untersucht, indem man in die Eprouvette einige Tropfen konzentrirten Ammoniak zusetzt, umschüttelt und darauf in das Gemisch einen möglichst kleinen Tropfen einer konzentrirten Nitroprussidlösung zufügt und beobachtet: Wenn der untersuchte Spiritus rein ist, so bildet sich bei den obigen Verhältnissen eine blassrote Färbung, welche durch das weitere Zutropfen von der Nitroprussidlösung etwas intensiver wird. Ist aber der fragliche Alkohol methylalkoholhaltig gewesen, so entsteht durch den ersten

Tropfen Nitroprussidlösung eine rein blaue Färbung, welche nach einiger Zeit ins Gelb übergeht. Ein weiterer Tropfen der Prussidlösung erzeugt von neuem blaue Färbung u. s. w. Ebenso verhalten sich die Destillate in allen anderen Eprouvetten, und zwar ist die blaue Färbung um so intensiver, je später die Fraktionen aufgefangen sind.

Azeton liefert mit Ammoniak und Nitroprussidnatrium eine ziemlich starke violette Färbung, ähnlich dem Hofmann's Violett, welche in einiger Zeit rotbraun wird. Die Anwesenheit des Azetons hindert nicht die Bildung des blauen Farbstoffes durch Nitromethan.

Oben wurde erwähnt, dass bei den beschriebenen Farbreaktionen der Ammoniak durch Alkalien ersetzt werden kann. Die näheren Untersuchungen in dieser Richtung haben folgende Resultate geliefert: Nitromethan reagirt mit Nitroprussidnatrium in Anwesenheit von Alkalien auf dieselbe Weise wie in Anwesenheit von Ammoniak. Ein Ueberschuss von Alkalien—im Gegensatz zum Ammoniak, welcher die Reaktion nicht beeinträchtigt—hindert die Reaktion so weit, dass sie unter Umständen ausbleiben kann.

Nitroäthan bildet in Anwesenheit von Alkalien auch durch den ersten Tropfen der Nitroprussidlösung eine intensiv weinrote Färbung, welche ganz ähnlich derjenigen ist, welche das Azeton unter denselben Umständen erzeugt.

Aus diesem Grunde ist zu der obigen Farbreaktion der Ammoniak den Alkalien vorzuziehen.

(*Auszug*)

UEBER RIZINUSÖLSÄURE

VON PROF. DR. B. RASSOW

Leipzig, Germany

(Nach Versuchen von Dr. J. Rubinsky.)

1. Die Rizinusölsäure spaltet beim Erhitzen für sich Wasser ab; dabei geht die Azidität bis auf 50% des ursprünglichen Wertes herunter; flüchtige Zersetzungsprodukte entstehen bei Temperaturen bis zu 150° nicht.

Rizinusölsäure liefert beim Erhitzen in Gegenwart von Spuren von Schwefelsäure Produkte, deren Azidität schliesslich nur 25% des Ausgangsmaterials beträgt; die Azidität 0 wird aber nie erreicht.

3. Die Produkte der Erhitzung von Rizinusölsäure sind sogenannte Polyrizinusölsäuren, das heisst Estersäuren, bei denen das alkoholische Hydroxyl des einen Molekuls mit dem Carboxyl eines anderen verestert ist. Es wurde nachgewiesen, dass alle anderen Umwandlungsmöglichkeiten ausgeschlossen sind.

4. Das Erhitzungsprodukt ist nicht einheitlich, sondern ein Gemisch von schwer oder gar nicht trennbaren Polyrizinusölsäuren mit mehr oder weniger unverändertem Ausgangsmaterial.

5. Die hochmolekularen Poly-Säuren sind in Alkohol unlöslich; ihre Bariumsalze sind bernsteinartig und lösen sich in Aether.

Die niedrigmolekularen Poly-Säuren lösen sich in Alkohol, ihre Bariumsalze sind in Aether schwer löslich.

Eine genaue Trennung der einzelnen Polyrizinusölsäuren gelingt nicht.

6. Von den verwendeten Katalysatoren haben Neutralsalze wenig Einfluss, wenn sie nicht Säuren abspalten, ebensowenig organische Säurechloride. Organische Basen wirken als negative Katalysatoren.

7. Rizinelaidinsäure verhält sich ähnlich wie Rizinusölsäure, wird aber durch Erhitzen leichter zersetzt.

STUDIES IN ESTERIFICATION V[1]: THE ESTERIFICATION OF AMIDES AND THIO-AMIDES AND THE FORMATION OF DITHIO-ESTERS

E. Emmet Reid
Jersey City, N. J.

In previous papers it has been shown that, as regards esterification, benzamide is the analogue of benzoic acid[2] and that mercaptan is the analogue of alcohol.[3] In the present paper it is shown that benzamide may be esterified by mercaptan and thiobenzamide by alcohol and mercaptan.

We have the following group of analogous reactions.

1 $C_6H_5COOH + HOC_2H_5 \underset{1}{\overset{4}{\rightleftarrows}} C_6H_5COOC_2H_5 + H_2O$

2 $C_6H_5COOH + HSC_2H_5 \underset{25}{\overset{1}{\rightleftarrows}} C_6H_5COSC_2H_5 + H_2O$[4]

3 $C_6H_5COSH + HOC_2H_5 \underset{0}{\overset{1}{\rightleftarrows}} C_6H_5COOC_2H_5 + H_2S$[5]

4 $C_6H_5CONH_2 + HOC_2H_5 \underset{170}{\overset{1}{\rightleftarrows}} C_6H_5COOC_2H_5 + NH_3$[6]

5 $C_6H_5CONH_2 + HSC_2H_5 \underset{17000}{\overset{1}{\rightleftarrows}} C_6H_5COSC_2H_5 + NH_3$

6 $C_6H_5CSNH_2 + HOC_2H_5 \underset{170}{\overset{1}{\rightleftarrows}} C_6H_5CSOC_2H_5 + NH_3$

7 $C_6H_5CSNH_2 + HSC_2H_5 \underset{17000}{\overset{1}{\rightleftarrows}} C_6H_5CSSC_2H_5 + NH_3$

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[1] Am. C. J. *41*, 483; *43*, 498; *45*, 38 and 479.

[2] Ibid. *41*, 483.

[3] Ibid. *43*, 490.

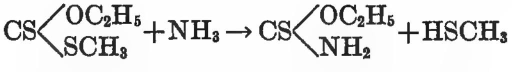
[4] Ibid. *43*, 502.

[5] Ibid. *43*, 494.

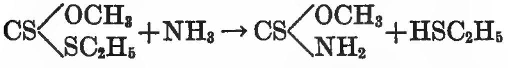
[6] Ibid. *45*, 511.

All of these reactions may be readily formulated in terms of Henry's addition hypothesis.[1] All of them, with the possible exception of No. 3, are reversible, but the equilibrum points are very differently placed. For unit quantities the forward velocity in reaction 1, as is well known, is 4 times as great as the backward. Adopting the notation used in a previous article[2] this is written $\overset{\overset{4}{\rightarrow}}{\underset{1}{\leftarrow}}$. The relative forward and backward velocities given in reactions 2, 3, and 4 are those found in previously published experiments. By the principle of interdependence of limits,[3] the backward velocity in reaction 5 should be 170 x 100 = 17,000 times the forward velocity. The same relative velocities would appear in reaction 7, while in reaction 6 the relative rates would be 170: 1 as in reaction 4. As is well known amides are readily prepared by heating esters with alcoholic ammonia, while only in presence of acid is benzamide easily or largely esterified.[4] Acids and amides of the benzoic series have been chosen for the work, but they are regarded as typical of acids and amides in general provided there are no special properties to interfere with the reactions.

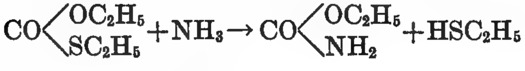
Comparing reactions 4 and 5, we conclude that ammonia would replace mercaptan in ethyl thiolbenzoate much more rapidly and completely than it would drive out alcohol from ethyl benzoate. In case of mixed esters this has been found to be true, the mercaptan half of the molecule being completely transformed before the alcohol half is touched. Thus Salomon[4] found that

8 

$$CS\begin{matrix}\diagup OC_2H_5\\ \diagdown SCH_3\end{matrix} + NH_3 \rightarrow CS\begin{matrix}\diagup OC_2H_5\\ \diagdown NH_2\end{matrix} + HSCH_3$$

9 

$$CS\begin{matrix}\diagup OCH_3\\ \diagdown SC_2H_5\end{matrix} + NH_3 \rightarrow CS\begin{matrix}\diagup OCH_3\\ \diagdown NH_2\end{matrix} + HSC_2H_5$$

10 

$$CO\begin{matrix}\diagup OC_2H_5\\ \diagdown SC_2H_5\end{matrix} + NH_3 \rightarrow CO\begin{matrix}\diagup OC_2H_5\\ \diagdown NH_2\end{matrix} + HSC_2H_5$$

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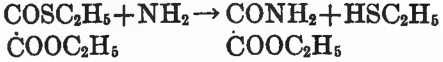
[1] Ber. d. chem. Ges. 10, 2041.

Am. C. J. *43*, 490.

[2] Ibid. *43*, 502. [3] Ibid. *45*, 479. [4] Ibid. *41*, 483.

[5] Jour. pr. Chem. (2) *8*, 114 and *6*, 433.

and Morley and Saint[1] found that

11 

$$\underset{COOC_2H_5}{COSC_2H_5} + NH_2 \rightarrow \underset{COOC_2H_5}{CONH_2} + HSC_2H_5$$

In a previous paper[2] an experiment was given in which ethyl benzoate saturated with dry ammonia was heated to 200° for 14 hours and showed only partial transformation the equilibrium point being reached only after much longer heating. Thus ammonia reacts with ethyl benzoate only slowly at 200° while the following experiment shows that ethyl thiolbenzoate is readily acted upon even at 20°.

Ethyl thiolbenzoate was weighed into a tube and saturated with ammonia which had been dried over lime and caustic soda, and the tube sealed. At room temperature a precipitate appeared after several hours and crystals formed over night. After 8 hours the crystals filled one third of the liquid and did not seem to increase during several days. To insure the completion of the reaction to the limit, the tube was heated to 100° for 15 hours. On opening no pressure was found, and moist litmus paper showed only a tinge of blue. The mercaptan was identified by distilling into lead acetate solution. The mixture of amide and ester was poured into water and titrated using cochineal as indicator, but the amount of ammonia present was too small to affect the indicator. The mixture was distilled with steam, the residue evaporated in a tared dish and weighed as amide, the ester extracted from the distillate, dried and weighed. The numerical data are given in grams and in millimoles.

Ethyl thiolbenzoate taken	5.6899 g. or	34.13	m. moles	
Ammonia taken	0.1272 g. "	7.47	"	
Ester left after total action		26.66	"	or 4.427 g.
Ester recovered				or 4.468 g.
Benzamide calculated		7.47	"	or 0.905 g.
Benzaimde found				0.915 g.

This benzamide once crystallized from water had m. p. 125.5°. This experiment shows that the reaction is practically complete and that the equilibrium point is far to one side. In order to approach the equilibrium point from the other side, several tubes containing benzamade and mercaptan were heated to 200° for some hours. The products were complex and were not suitable for quantitative work.

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[1] Jour. Chem. Soc. *43*, 400.

[2] Am. C. J. *45*, 511.

Since, as has been shown, benzamide is readily esterified according to reaction 4, in presence of hydrochloric acid which not only catalyzes the reaction but also combines with the liberated ammonia so that the reaction goes to completion, it was to be expected that hydrochloric acid would likewise accelerate the esterfication of benzamide by mercaptan accordng to reaction 5. A quantity of benzamide was sealed up wth some mercaptan which had been saturated at −20° with dry hydrochloric acid. The mixture was heated for several days to 100°. On opening the tube no hydrochloric acid was found and ammonium chloride and ethyl thiolbenzoate were identified. A similar experiment was tried with acetamide, with similar results, but the resulting ester did not seem so pure. Benzamide and acetamide readily form hydrochlorides when treated with hydrochloric acid in presence of mercaptan.

Matsui[1] found that alcoholic ammonia decomposes thion-ester even in the cold with great ease to give thion-amide. That is, the reversal of reaction 6 takes place readily. He found that thion-esters are readily transformed, with evolution of hydrogen sulphide, into oxygen esters by water, acids, alkalies, etc. It was expected that, in presence of hydrochloric acid, alcohol would react with thionbenzamide to give the thion-ester according to reaction 6. Much time was spent on a study of this, and many tubes were sealed up containing various mixtures and treated in different ways, but, while all of the mixtures yielded esters, by the time that the esters had been washed free from acid and other impurities they consisted mainly of ethyl benzoate. This is not surprising since, according to the experiments of Matsui, the thion-esters so readily exchange hydrogen sulphide for water.

The most interest attached to reaction 7 since, at the time that this work was taken up, the Summer of 1909, no dithio-ester had been made except among the carbonates which were formed by a

[1] Mem. Col. Sc. and Eng. Kyoto *1*, 285.

special reaction. Ethyl dithio-benzoate was prepared according to this reaction in September 1909. Since that time Bloch, Höhn, and Bugge[1] and Höhn and Bloch[2] have made dithio-acids by the condensation of aldehydes with hydrogen persulphide and have alkylated salts of these acids. Houben and Schultze[3] have recently alklyated salts of dithio-acids made according to the method of Houben and Pohl[4] by treating Grignard compounds with carbon bisulphide.

Dry hydrochloric acid combines readily with thiobenzamide and with other thio-amides. The compound with thiobenzamide is liquid at moderate temperatures but forms light colored, well formed, transparent crystals at low temperatures. When gaseous hydrochloric acid is passed over thiobenzamide the bright yellow needles melt into a viscous amber colored liquid much of which solidifies at low temperatures. Quantitative work showed that the hydrochloric acid taken up is, in this case, about 1.5 molecules while with other thioamides it is nearly one molecule. Acid is lost from some, at least, of these compounds in a current of dry air.

In the following experiments the thio-amide was weighed into a glass stoppered U-tube and dry hydrochloric acid passed through. In some cases the acid was displaced by dry air before weighing and in others in similar empty U-tube, through which the same current of gas was passed, was used as a tare. Entirely constant weights were obtained in no cases. In the case of thiobenzamide the viscous nature of the product formed prevents uniform and thorough action. In one experiment 0.7179 g. thiobenzamide was exposed to hydrochloric acid for 3 weeks and then dry air was passed for a short time. The gain in weight was 0.3048 g. or 1.6 mol. hydrochloric acid for 1 mol. of the thiobenzamide. In another case a U-tube containing 1.0528 g. thiobenzamide through which dry hydrochloric acid was passed, at intervals during three weeks, gained 0.4286 g. more than a similar U-tube used as a tare. This is 1.53 mol. In the case of thio-x-naphthoicamide the gain on exposure of 0.2433 g. to hydrochloric acid for several days, was 0.0554 or 1.18 mol., while for 0.3391 g. thio-o-toluic amide under the same treatment, the gain was 0.0787 g. or 0.96 mol. Considerable heat is evolved in all of these combinations.

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[1] Jour. Pr. Chem. (2) *82*, 473 (1910).

[2] Ibid. (2) *82*, 486 (1910).

[3] Ber. d. chem. Ges. *44*, 3226 (1911).

[4] Ibid. *39*, 3219 (1906).

To prepare ethyl dithiobenzoate, thiobenzamide is roughly weighed into a tube and saturated with dry hydrochloric acid 0°. Somewhat more than the calculated amount of mercaptan is added and the tube sealed. The mixture usually becomes homogeneous on warming to room temperature, but frequently deposits beautiful, well formed, transparent, rectangular crystals on cooling. These are sometimes as large as 3 x 6 mm. The mixture is kept at 25° for five weeks or more. The progress of the reaction may be judged by the accumulation of the precipitated ammonium chloride. On opening the tube some pressure is found and considerable hydrochloric acid is evolved. The product is mixed with redistilled light petroleum ether which mixes in all proportions with the ester, but leaves unchanged thiobenzamide and ammonium chloride, both of which are insoluble in petroleum ether. Much of the hydrochloric acid escapes on exposure to the air and the rest is washed out of the petroleum ether solution by shaking it with water containing a little sodium carbonate. The solution is dried over calcium chloride and the petroleum ether distilled off. The ester remaining is distilled in vacuum. In two preparations the attempt was made to hasten the process by heating the mixture to 100° for from 14 to 40 hours. In these cases the ammonium chloride formed rapidly and the ester seemed to be formed in abundance, resembling the usual product in appearance, but when it came to the fractionation, the product was found to be complex and to contain much high boiling material. It is known that dithiobenzoic acid readily polymerizes. However, when the reaction mixture is kept at 25°, the reaction though slow and, so far as tried, never complete, yet seems to be a clean one as no other products seem to be formed and the ester obtained boils quite constant. In the first preparation 28.6 g. thiobenzamide was used to 33 cc. mercaptan and although a considerable portion of the product was lost by an accident, 15 g. of ethyl dithiobenzoate was obtained as the main fraction, boiling within about 1° of

208° under 99 mm. This had d. $\frac{25}{25}$ of 1.1423. The last preparation boiled at 180° under 28 mm. and had d. $\frac{25}{25}$ 1.1477. The properties are given in tabular form along with those of ethyl benzoate and ethyl thiobenzoate.

Ethyl	Benzoate	Thiolbenzoate	Dithiobenzoate
B. p.	213.1$^{757mm.}$	253$^{763mm.}$	280?
d. $\frac{25}{25}$	1.0447	1.0971	1.1477
d. $\frac{25}{4}$	1.0417	1.0937	1.1439
Increase for 1 S	———	0.0524	0.0506
Apparent coef. expan. 0–25°	0.000861	0.000775	0.000699
Mol. Volume	144.07	151.51	159.28
Increase for 1 S	———	7.84	7.77
Viscosity at 25°	0.01909	0.02421	0.03117
Increase for 1 S	———	0.00510	0.00696
Fluidity at 25°	52.39	41.31	32.09
Decrease for 1 S	———	11.08	9.22

The figures for molecular volumes are of interest since in passing from the benzoate to the thiolbenzoate a hydroxyl oxygen is replaced by sulphur while in the next step a carbonyl oxygen is replaced. The increase of molecular volume is the same in both cases, hence if oxygen has two different atomic volumes according to its mode of combination, sulphur seems also to have two different atomic volumes and they seem to differ by the same amount that the oxygen values do. The fluidities are more nearly additive than the viscosities which agrees with the general conclusions of Bingham.

Ethyl dithiobenzoate is a thick oil, of a beautiful red color, with a rather pleasant odor resembling ethyl benzoate and thiolbenzoate. It is quite stable. A specimen of it was kept for over a year in a cork stoppered bottle with no apparent change, though at the end of that time it did not all distil properly and gave slightly low analytical results for sulphur. The ester passes over slowly with steam. A sulphur determination according to a slightly modified form[1] of the method of Morse and Gray[2] gave 34.94% sulphur instead of the calculated 35.20.

[1] Am. Chem. Jour. *47*, 416.

[2] Ibid. *35*, 451.

The most characteristic reaction is its easy transformation at room temperature, by alcoholic ammonia into thionbenzamide. The ester, to the amount of 0.2988 g., was weighed into a beaker and covered with alcoholic ammonia. After standing over night, the mixture was evaporated to dryness and 0.2326 g. of thionbenzamide was obtained instead of the calculated 0.2250 g.

Considerable time was spent upon the saponification of this ester in the hope of preparing the long sought thionbenzoic acid, $C_5H_6CS.OH$, which though described by Fleischer,[1] has probably not yet been made.[2] Some results have been obtained, but not conclusive. Houben and Schultze[3] obtain naphthoic acid as the final product of the saponification of the corresponding dithionaphthoic esters. Matsui[4] found the thion-esters unstable in the presence of oxygen compounds and the thion-acids are probably more unstable.

The observations here made on ethyl dithiobenzoate agree well with those made by Höhn and Bloch[5] on the same ester and with those made by these authors and by Houben and Schultze[6] on the corresponding methyl ester and on other esters of this class. It is of value to have a variety of methods for preparing compounds of this class, since one method may give good results in cases in which another fails. Since thio-amides are readily made from nitriles which are generally accessible, the present method would seem to be applicable in a number of cases. By this method the esters are obtained directly from stable well crystallized compounds. However, the present work was undertaken to complete the systematic study of a group of closely related reactions rather than to add to the number of organic compounds. The results show that reaction 7 is reversible and that the equilibrium point is far to one side as is the case with reactions 4, 5 and 6.

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[1] Am. Chem. (Liebig.) *140*, 236.

[2] Ber. d. chem. Ges. *15*, 861. Am. Chem. Jour. *43*, 491.

[3] Ber. d. chem. Ges. *44*, 3232.

[4] Loc. cit.

[5] Loc. cit.

[6] Loc. cit.

MARGARIC ACID AND ITS RELATIONS TO PALMITIC & STERIC ACIDS

R. F. Ruttan
McGill Univesity, Montreal, Canada

Introduction

Chevreuls was the first to use the name "Margaric acid." It is found in his early researches on the constitution of fats and soap formation, published in 1811. From pigs fat he separated two fats of different melting points, the solid one he called "Stearin" and the liquid fat "Elæin." The acid obtained from the soap of the former he named "Acide Margarique" and from the oily fat he obtained an acid called by him "Acide Oleique." He subsequently resolved a large number of animal and vegetable fats into these acids and described Margaric acid as the characteristic acid of Spermaceti. In 1820 he divided Margaric acid into two acids of different melting points "Acide Margarique" and "Acide Stearique."[1]

Heintz in 1852 and Berthollet subsequently demonstrated that the acid called Margaric by Chevreuls was a mixture of Stearic and Palmitic acids. This eutectic mixture cannot be separated by crystallization but Heintz separated the acids by recrystallization of their magnesium salts.

The true Margaric acid $C_{17}H_{34}O_2$ has been prepared. Heintz probably obtained it in 1857. By heating potassium cetyl sulphate with potassium cyanide to 200° he obtained an impure cetyl cyanide which by boiling with alcoholic potash gave among other products a soap from which he separated two acids, one of these melted at 59.9°C and gave an analysis $C_{34}H_{34}O_4$. This was called by him Margaric acid.

Krafft[2] also obtained small quantities of the acid in 1880. He distilled at 110 mm. pressure a mixture of Barium Stearate and

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[1] Recherches Chemiques sur les corps gras d'origine animale (Paris 1823).

[2] Annales de chem et de physique (7) 24, 454.

Barium Acetate. The resulting mixed Ketone $C_{17}H_{35}COCH_3$ having the M. P. 55.5°C was carefully oxidized by potassium bichromate and dilute sulphuric acid with the production of Margaric and acetic acids. He also prepared the sodium and silver salts but no esters. Repeating this process it was found that a yield of ester not more than ten per cent was obtained and on oxidation a very small yield of a solid fat acid was given which was a mixture from which Margaric acid could only with difficulty be separated.

The only practical preparation and careful study of Margaric acid hitherto recorded is by Le Sueur in 1904.[1] He prepared the acid in the course of an interesting study of the effect of heat upon the alpha hydroxy derivatives of the higher fatty acids. He first prepared alpha brom-stearic acid by the Hell and Sadonsky's method, converted this into the alpha hydroxy acid by action of dilute aqueous potassium hydrate at 100° C and on heating this dry acid to 270° C he obtained Margaric aldehyde with evolution of CO and formic acid. The Margaric aldehyde on oxidation with potassium permanganate gave Margaric acid. He further prepared the silver salt of the acid the methyl and ethyl esters, the alpha brom and alpha hydroxy derivatives and the amide.

Regarded simply as a method of preparation of Margaric acid, this process is certainly complicated, as it is necessary to prepare and separate three derivatives of the available material, stearic acid before obtaining the desired product, margaric acid.

By the an application of Grignard reaction this acid has been prepared by the writer conveniently and directly from cetyl iodide or bromide.

Among the numerous applications of this reaction comparatively few studies have been made of the action of carbon dioxide upon the haloid magnesium compounds in the Grignard reagent. It seemed interesting to ascertain whether cetyl iodide would with the constituents of the Grignard reagent take up carbondioxide and produce margaric acid. It seemed probable from Grignard's researches[2] that the magnesium in presence of anhydrous ether would unite with the cetyl iodide to form the organo metallic compound $C_{16}H_{33}MgI$ and this might absorb carbon dioxide and form such an intermediate unstable substance as $C_{16}H_{33}COOMgI$ which on acidification with hydrochloric acid would give Margaric acid $C_{16}H_{33}COOH$ and MgICl.

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[1] Trans. Chem. Soc. 1904, 827.

[2] Annales de chem. et de physique (7) 24, 454.

A method was devised after a few preliminary experiments by which the Grignard reaction was applied as described above and gave 60–70% of the theoretical yield of Margaric acid. The chief difficulty was found not in obtaining the reaction but in separating the acid from the other constituents resulting from the reaction.

A considerable quantity 200–300 grams having been prepared by this method, a study of the relations of this acid to those well known fat acids adjoining it in the homologous series viz. Palmitic and Stearic has been made.

Margaric acid has not yet been found in any natural fat, unless we accept the statement that it occurs in adipocere as ammonium margarate. (Ebert B. 8.775). Theoretically it is of interest as the intermediate member of the acid series between palmitic and stearic acids having an uneven number of carbon atoms. It is probably more than a coincidence that in the processes of plant and animal metabolism the fats stored up contain almost exclusively acids with an even number of carbon atoms.

In this paper the constants and the known derivatives of margaric acid are compared in tabular form with those of palmitic and stearic acids. Incidentally, several of the constants of the latter acids have been carefully redetermined and others added where it seemed desirable.

EXPERIMENTAL

Preparation of Margaric acid by the Grignard reaction

The reaction is conducted in a well dried 1 litre distilling flask, the neck of which is bent upwards and fitted to a long 4 tube reflux condenser. To the top of the condenser is attached a U shaped chloride of calcium tube to exclude moisture.

In the neck of the flask, a double bored stopper carries a tube to the bottom of the flask through which the carbon dioxide is introduced, this tube is about 1 cm in diameter where it dips below the liquid, to prevent blocking by the solid products of the reaction. The cetyl iodide is introduced by a short stemmed 100 c.c. separating funnel with stopper which is inserted through the other opening in the cork of the flask.

The flask and connections are placed upon a water bath, 400 c.c. of anhydrous ether and about 5 grammes of polished magnesium ribbon or bright granulated magnesium are first introduced and the flask closed; 70.4 grammes of dry cetyl iodide are then dropped in by aid of the separating funnel, about half that quantity at first with a crystal of iodine to act as a catalyser the balance added more slowly about 1 c.c. at a time, after the reaction begins. The reaction first shows itself by a bleaching of the iodine and a gentle ebullition of the ether in the vicinity of the magnesium. The reaction is continuous for about one hour but never becomes violent; the mixture turns opalescent and carries black particles of the traces of iron in the magnesium. When the reaction nearly ceases the contents of the flask are heated for another hour, the ether being kept in vigorous ebullition. If the liquid be now allowed to cool a copious precipitate of the organo metallic compound separates in bright mica like crystals. About 400 c.c. more of ether are now gradually added as required, to maintain the contents in fluid form while the carbon dioxide is passed through the mixture. As the contents of the flask becomes thick it should be shaken occasionally and the temperature raised again to the boiling point of the ether. A slow stream of carbon dioxide should pass for from 3 to 4 hours to give good results. The carbon dioxide should be washed and *thoroughly dried* by a series of calcium chloride tubes and sulphuric acid.

When the reaction is finished, the flask is well cooled, broken ice or snow slowly added with dilute solution of hydrochloric acid until a faint but permanently acid reaction is obtained. The thick ethereal mixture is washed with cold water and filtered to remove most of the hydrocarbon. A portion of the ether is distilled off the filtrate, and again filtered after cooling. The last filtrate containing the margaric acid, some hydrocarbon together with undecomposed cetyl iodide is evaporated to dryness, washed with warm diluted alcohol in which the hydrocarbon is almost insoluble, but which takes up the soluble acid and cetyl iodide. The alcohol is distilled off and the residue saponified; the dry powdered soap may be extracted in a Soxhlet or the aqueous solution repeatedly washed with ether to remove the cetyl iodide, traces of cetyl alcohol and any remaining hydrocarbon. The acid is now set free by warm dilute sulphuric acid in a beaker, the solid acid removed after cooling, washed with water and recrystallized from alcohol. By washing the hydrocarbon filtered off at different stages with dilute warm alcohol, more acid can be recovered. It was found that 35.2 grms. of the iodide yielded 19 grms. of acid having a melting point of 58° C this yielding 13 grms. of pure acid; theory requires 27 grms.

Ditria-contane or Dicetyl. The hydrocarbon obtained as a by product was purified by recrystallization from ether and was identified as Dicetyl $C_{32}H_{66}$ formed by the action of magnesium on the iodide $2\ C_{16}H_{33}I + Mg = C_{32}H_{66} + MgI_2$. It crystallizes from ether or hot alcohol in shining white waxy plates, melting at 70.5° C and has a refractive index of 1.4334 at 72° C. It is almost insoluble in cold alcohol and petrolic ether but very soluble in hot ether. It is somewhat soluble in the soaps of margaric acid from which it is extracted with difficulty. The slightest trace of moisture in the reacting mixture greatly increases the amount of this hydrocarbon formed. It is essential therefore to especially dry both the cetyl iodide and the carbon dioxide to minimise the formation of this hydrocarbon which is removed from the mixture with such difficulty.

Margaric acid. This acid has a habit of crystallization from dilute alcohol very similar to that of palmitic and stearic acid i. e. in thin, white, bulky shining plates.

It melts between 59.9° C and 60° C corrected and solidifies at 58.8° C.

At its melting point its specific gravity is 0.8532.

Its coefficient of expansion is 6.65×10^{-4} between 60° and 80° C.

Its solubility in absolute alcohol, grams in 100 grms. of alcohol is: @ 0°C–1.53 grms. @–5.4° C.–2.42 grms. @10° C–4. .12 grms. @15°–6.72 grms. @ 21° C–13.4 grms. @28° C–32.14 grms. (See diagram)

Its refractive index @ 60° C is 1.4342.

Salts of Margaric acid. The alkaline salts and those of the alkaline earths were not prepared in a pure form. The Calcium, Barium, Lead and Magnesium soaps are quite insoluble in water and all undergo partial hydrolysis.

Ammonium margarate may be obtained in a crystalline form by saturating a solution of the acid in absolute alcohol with dry ammonia. The crystals formed on cooling a solution in warm absolute alcohol are light feathery transparent crosses.

Silver Margarate. This salt was obtained in a pure crystalline form by slowly adding a warm alcoholic solution of silver nitrate to a warm nearly saturated solution of ammonium margarate. On cooling in the dark, the silver salt is precipitated in fine white prisms, striated parallel to the long axis of the crystal.

This salt dried in vacuo, in absence of light, was used to determine the *Molecular weight* of the acid.

0.5155 silver salt gave 0.1478 Ag or 28.67%

0.5276 silver salt gave 0.1513 Ag or 28.68%

Theory. $C_{17}H_{33}O_2Ag$ gives silver — 28.65%.

Methyl Margarate. This ester was prepared by boiling under reflux condenser a mixture of silver Margarate and methyl iodide in equivalent proportions diluted with several volumes of ether.

It is extremely soluble in most organic solvents and crystallizes from cold dilute alcohol in small waxy scales melting at 29° C.

Ethyl Margarate. This was prepared by the action of ethyl iodide upon the silver salt under conditions similar to those employed in the preparation of the methyl ester. It crystallizes with difficulty from very cold dilute alcohol in small waxy plates melting at 27.5° C.

Glycol esters. The mono Glycol Margarate or the hydroxy ethyl ester $C_2H_4OHC_{16}H_{33}O_2$ and the Glycol dimargarate or the ethylene Margarate $C_2H_4(C_{16}H_{33}O_2)_2$ were prepared by heating a mixture of the acid and glycol to 180° C. for 5–6 hours. The temperature was kept constant by employing a Victor Meyer's constant temperature drying bath heated by the vapor of boiling aniline (182° C). The mixture which contained glycol in a slight excess of the theory, was continually and rapidly stirred by a platinum stirrer rotated by a hot air motor. Both esters were formed and were easily separated by fractional crystallization from dilute ethyl alcohol, the dimargarate being much the less soluble of the two.

Glycol Mono margarate is very soluble in dilute alcohol from which it crystallizes with difficulty in pearly scales when cooled to 0° C. M. P. 53.2° C.

The dimargarate is more easily crystallized from alcohol in glistening plates which melt at 70.4° C.

(NOTE.) The details of the above method and apparatus will appear shortly in a paper on the "Glycol Fats" now being prepared for Jour. Am. Chem. Soc.

A comparison of the chemical and physical properties of Palmitic, Margaric and Stearic acids

In the accompanying table are gathered for easy reference the physical and chemical constants of these three allied acids.

Those constants, not determined or carefully redetermined by the author are credited as accurately as possible to the proper authority.

It is to be noticed that in almost all determinations, the constants of margaric acid and its various esters and derivatives lie between those of palmitic and stearic acids, i. e. the majority of these constants are more or less functions of the molecular weight of the acid. To this generalization regarding the relations of margaric acid, there are four well marked exceptions viz. its melting point, its index of refraction, its solubility in absolute alcohol and its boiling point under diminished pressure.

It is well established that the melting point of normal acids of the series $C_2H_{2n}O_2$ having an odd number of carbon atoms always lies lower than that of the homologue next below it.

Refractive Indices. On determining the refractive indices of these acids, it was observed that those of Palmitic and Stearic as shown above, are almost identical, differing only in the fourth decimal place by two units, while the refraction of Margaric acid is distinctly higher than that of Palmitic.

As the writer's observations were made with a simple form of Zeiss Refractometer and the results unexpected, samples of the acids were sent to Mr. A. McGill of the Department of Inland

Revenue, Ottawa, who kindly repeated and confirmed the writer's results, using the latest improved form of Zeiss Refractometer.

	Palmitic acid	Margaric acid	Stearic acid
Formula	$C_{16}H_{32}O_2$	$C_{17}H_{34}O_2$	$C_{18}H_{36}O_2$
Molec. weight	256	270	284
Melting point	62.2	59.9	69.3
Sp. gr. at M. P	0.8553	0.8532	0.8473
Molec. volume	299.3	316.4	335.1
Coef. of expansion	$6.89\mathrm{x}10^{-4}$	$6.65\mathrm{x}10^{-4}$	$6.65\mathrm{x}10^{-4}$
Index of refraction	1.4324	1.4342	1.4322
Sol. in 100 grms.			
Absolute alcohol @ 0° C.	1.45 grms.	1.53 grms.	0.37 grms.
" " @ 5° C.	2.0 "	2.1 "	0.51 "
" " @ 10	4.0 "	4.12 "	1.1 "
" " @ 15	6.5 "	6.72 "	1.6 "
" " @ 20	9.9 "	10.1 "	2.5 "
" " @ 25	16.8 "	20.1 "	4.9 "
" " @ 28	29.0 "	32.0 "	6.0 "
" " @ 36	81.0 "	— "	20.0 "
Boiling point	[1]268.5°C(100mm)	[1]227°C(100mm)	[1]291°C(100)
Methyl ester M. P	[2]28	[4]29	[3]38
Ethyl ester M. P.	[5]24	27.5	[6]33.7
Hydroxy ethyl ester M. P.	51.5	53.2	58.5
Ethylene ester M. P	68.5	70.4	75.8
Acide amide M. P.	[4]106	[4]106	[4]109
α Brom. acid M. P	[4]51.5	[4]52.5	[4]60.61
α Hydroxy acid M. P.	[4]86.5	[4]89	[4]91.92

[1] Krafft B. 12.1760.

[2] Berthelot J. 1853. 502.

[3] Hanhart J. 1858. 301.

[4] Le Sueur Trans. Chem. Soc. 1904, 827.

[5] Heintz J. 1853, 447.

[6] Heintz J. A. 92. 295.

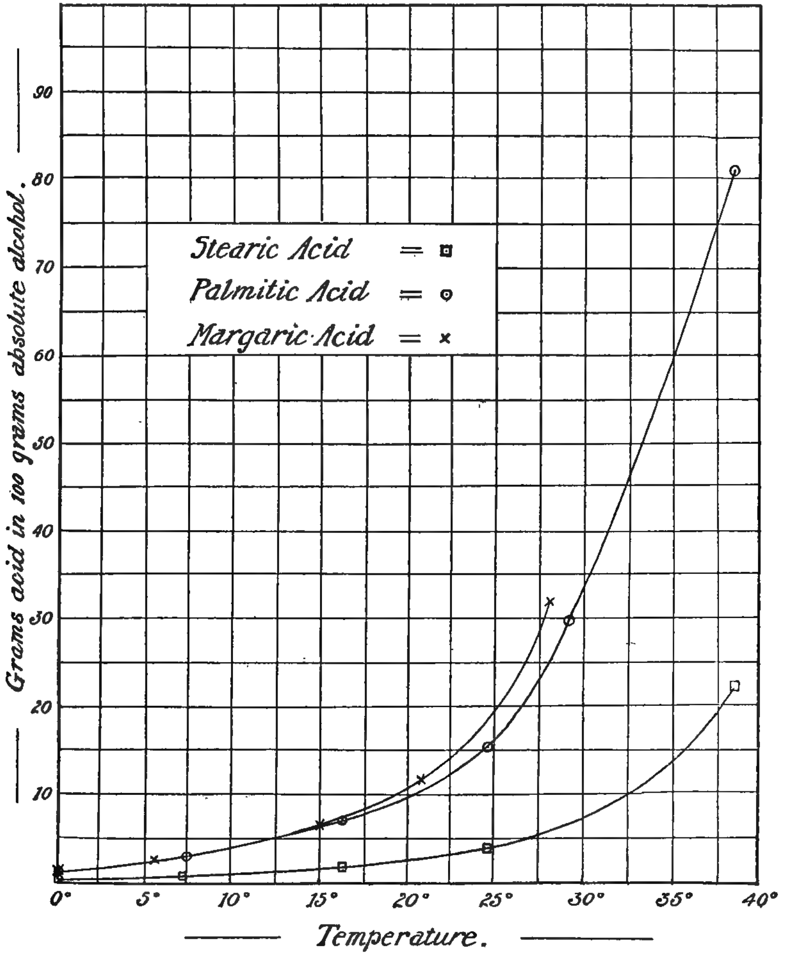
A eutectic mixture of palmitic & stearic acids in the proportion of 8 or 9 of Palmitic to 1 of Stearic acid crystallized from alcohol with a melting point similar to that of Margaric acid, viz. 59–60° C.

This mixture gave a refractive index higher than that of Palmitic acid and almost identical with that of Margaric viz. 1.4340.

The refractive indices of these acids were all determined at temperatures as near as possible to their melting points,—usually less than one degree above.

It would be interesting to find whether the refraction of other acids of this series with an odd number of carbon atoms was higher than that of the acid next lower in the series.

Solubility in absolute alcohol. The solubilities of the acids in absolute alcohol (at 15.5° C sp. gr. 0.79451 = 99.86%) at varying temperatures were carefully determined. The alcohol was saturated at a few degrees above that at which the observation was to be made and kept at the temperature of observation for from



5 to 6 hours; about 10 c.c. of the clear supernatant solution were drawn off into the weighing bottle, weighed, the alcohol evaporated and the residual acid dried to constant weight in an atmosphere of carbon dioxide. The results are stated in grammes of acid dissolved in 100 grammes of alcohol. All determinations were made in duplicate and gave concordant results.

The experimental data from which the solubility curves of Palmitic and Stearic acids in the above diagram were plotted are as follows:—

Temperature	Palmitic acid Grms. per 100 grms. alcohol	Stearic acid grms. per 100 grms. alcohol
0° C	1.449	0.373
7.4° C	3.087	.773
16.2° C	7.523	1.832
24.6° C	15.577	4.073
28.8	29.879	5.971
38.6	81.110	22.511

The determinations from which the solubility curve of Margaric acid is drawn are given above.

The solubilities for each rise of 5° C given in the table page (438) where not directly determined, were obtained by interpolation from the solubility curves.

It will be seen that while margaric acid at temperatures below 15°–16° C is very slightly more soluble than Palmitic acid, the curves practically coinciding, above 16° C the solubility of margaric acid increases much more rapidly as the temperature rises. It would seem that the relative solubility of Margaric acid is, at these higher temperatures, influenced by its lower melting point.

It will always be very difficult to detect margaric acid in presence of palmitic or to separate a mixture of the two set free from a fat owing to this similarity in their solubilities in alcohol.

The solubilities of these acids in dilute alcohol, ligroin and ether at room temperature were also found to be quite similar.

The boiling point of Margaric acid under diminished pressure evidently follows its lower melting point.

Densities of the fused acids. The densities of Palmitic and

Stearic acids at temperatures near their melting points were determined in 1882 by F. Krafft.[1] He obtained for Palmitic acid 0.8527 and for Stearic acid 0.8454, values which are regularly quoted.

In as much as the specific gravity of Margaric acid was found to be greater than that reported by Krafft for Palmitic acid, the densities of both Palmitic and Stearic acids were carefully redetermined and at the same time the coefficients of expansion of the fused acids were obtained.

The determinations were made in a bulb tube of about 3 c.c. capacity on a capillary stem carefully calibrated. The observations were made on the tube suspended with a small accurate thermometer in the inner narrow chamber of a double walled glass vessel. The outer chamber was connected with a reflux condenser and in it was boiled some liquid such as –chloroform, methyl alcohol, benzol or water whose vapor gave the desired temperature. The results were recorded when the temperature and the readings on the capillary stem of the tube remained constant for 20–30 minutes and the readings for each acid were taken at three temperatures.

On plotting the readings or the calculated densities against temperature, there was little or no deviation from a straight line. The density at the lowest temperature was determined within a few degrees of the melting point of the acid and the highest 15–20 degrees higher.

The specific gravity at the exact melting point was found by extrapolation.

The densities obtained at the different temperatures calculated to water at 4° C, which the densities at the melting points were determined are as follows for the three acids:—

Palmitic acid.	0.8534 @ 64.9° C
	0.8443 @ 78.2° C
	0.8433 @ 79.6° C
(By extension)	0.8553 @ 62.2° C
Margaric acid	0.8527 @ 60.6° C
	0.8512 @ 64.3° C
	0.8411 @ 78.1° C

---

[1] Berichte 15, 1728.

(By extension)	.8532 @ 59.9° C
Stearic acid	0.8418 @ 78.0° C
	0.8399 @ 81.1° C
	0.8276 @ 99.5° C
(By extension)	0.8375 @ 69.3° C

It will be seen that Krafft's values for the specific gravities of Pamitic and Stearic acids taken at their melting points, are distinctly too low.

The densities of these fused acids between the temperatures of observation, may be calculated from the following formulae where *it* is the desired temperature:—

Palmitic acid	$D = 0.8533 + 6.89 \mathrm{x} 10^{-4} \times (62.2 - t)$
Margaric acid	$D = 0.8532 + 6.65 \mathrm{x} 10^{-4} \times (59.9 - t)$
Stearic acid	$D = 0.8475 + 6.5\ \mathrm{x} 10^{-4} \times (69.3 - t)$

The Palmitic and Stearic acids employed were the purest Kahlbaum's acids recrystallized several times from alcohol to the above melting points.

I wish to express my thanks to my colleague Dr. D. McIntosh for kind assistance in the density determinations.

(*Abstract*)

THE MOLECULAR REARRANGEMENT OF TRIPHENYLMETHYLHYDROXYLAMIN

JULIUS STIEGLITZ, GUY REDDICK AND PAUL LEECH
University of Chicago, Chicago, Ill.

Triphenylmethylhydroxylamin has the structure assigned by Stieglitz to an assumed intermediate product, $(C_6H_5)_2CCl$ (NHOH); of benzophenone oxim and hydrogen chloride in the molecular rearrangement of the oxim by means of phosphorus pentachloride. Triphenylmethylhydroxylamin was found to undergo exactly the same rearrangement as the oxim when it is treated with phosphorus pentachloride: the product of the rearrangement, phenylimido benzophenone, was identified by comparison with synthetic phenylimido benzophenone, prepared from anilin and benzophenone dichloride, and by identifying its decomposition products, anilin and benzophenone, when it was hydrolyzed by treatment with hydrochloric acid.

(*Abstract*)

THE MOLECULAR REARRANGEMENT OF TRIPHENYLMETHYLBROMAMIN

JULIUS STIEGLITZ AND ISABELLE VOSBURGH
The University of Chicago, Chicago, Ill.

Triphenylmethylbromamin was proved to suffer a molecular rearrangement into phenylimido benzophenone, with the loss of hydrobromic acid, when subjected to the action of soda-lime at 100°–120° when acted upon by a hot solution of sodium methylate in methyl alcohol solution. The product of the rearrangement was identified by comparison with synthetic phenylimido benzophenone and by the identification of its decomposition products, anilin and benzophenone, when acted upon by hydrochloric acid. The salt produced by the action of the bases can only be a salt containing the metal attached to nitrogen and the salt or its anion must be the substance whose decomposition leads to the rearrangement.

(*Résumé*)

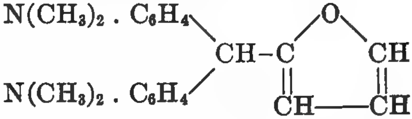
SUR QUELQUES DÉRIVÉS DU DIPHÉNYLFURYL-MÉTHANE

DR. V. VESELÝ

Laboratoire de chimie organique de l'Ecole polytechnique tchèque, Prague

Le furfurole et ses homologues, contenant un groupe aldéhydique, sont des combinaisons éminément apte à réagir, et ce fut déjà *O. Fischer* (Liebig's Annalen 206, i4i) que se servit du furfurole pour la préparation d'une leucobase correspondante à un colorant de la série du triphénylméthane, en condensant l'aldéhyde en question avec la diméthylaniline:

$C_5H_4O_2 + {}_2C_6H_5N(CH_3)_2 =$



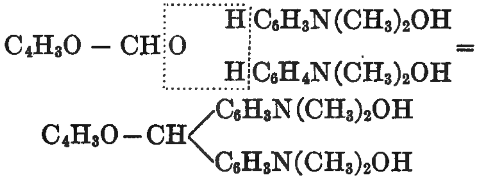
Comme l'agent de condensation il employa le chlorure de zinc fondu.

Oxydée par la chloranile ou par le peroxyde de plomb, la solution de ce corps prend de suite une coloration vert foncé, qui ne résiste que très peu à la lumière.

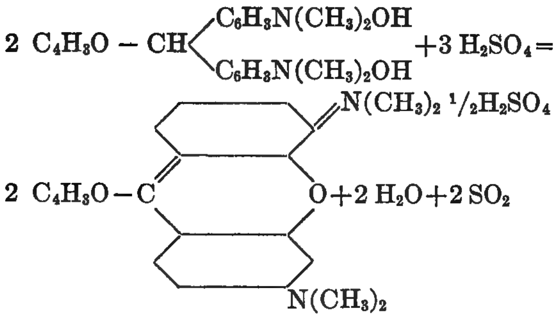
Partant du méthylfurfurole, nous l'avons utilisé pour la préparation d'une leucobase homologue qui a été obtenue par le même procédé en état cristallin. Ce corps soumis à l'action oxydante de la chloranile se transforme en matière colorante bleue.

Occupés de l'étude des rosamines, il nous paraissait intéressant d'essayer de condenser le furfurole et le méthylfurfurole avec le diméthylm-aminophénol et nous avons eu l'avantage d'arriver ainsi aux leucobases qui, soumises à l'action de l'acide sulfurique concentré, fournirent des matières colorantes de constitution an analogue à celle des pyronines et des rosamines.

Voici les équations qui expliquent la formation de ces corps:



$$C_4H_3O-CH\boxed{O\;\begin{matrix}H\\ \\ H\end{matrix}}\begin{matrix}C_6H_3N(CH_3)_2OH\\ \\ C_6H_4N(CH_3)_2OH\end{matrix}=C_4H_3O-CH\begin{matrix}\diagup C_6H_3N(CH_3)_2OH\\ \diagdown C_6H_3N(CH_3)_2OH\end{matrix}$$



$$2\ C_4H_3O-CH\begin{matrix}\diagup C_6H_3N(CH_3)_2OH\\ \diagdown C_6H_3N(CH_3)_2OH\end{matrix}+3\ H_2SO_4=$$

Nous avons obtenu ces colorantes sous forme de sels doubles avec le chlorure de zinc, à l'état cristallin de couleur noire et à éclat métallique. Ils teignent la soie en mauve foncé, qui est assez stable à la lumière. La matière colorante obtenue par le méthylfurfurole a une nuance un peu plus rougeâtre que celle dérivée du furfurole.

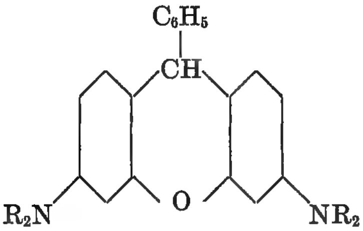
(Résumé)

CONTRIBUTIONS À L'ETUDE DES ROSAMINES

Dr. V. Vesely

Laboratoire de chimie organique, de l'Ecole polytechnique tchéque, Prague

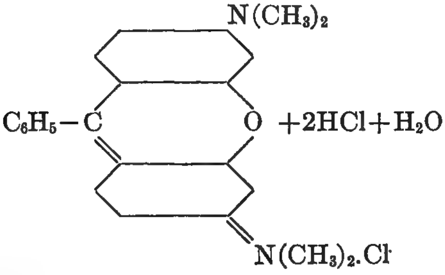
Les matières colorantes dérivées des diaminoxanthènes alcoylés (1) et qui sont connues sous le nom de rosamines, ont été préparé pour la première fois par *Heumann*, qui avait obtenu un représentant de cette classe en condensant le trichlorure de benzényle avec le diméthyl-m-aminophénol.—



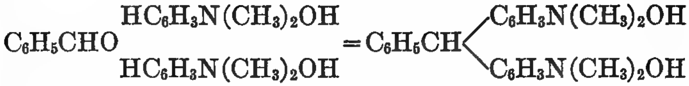
I

Cette réaction peut être exprimé au moyen de l'équation suivante:

$$C_6H_5CCl_3+2\,C_6H_4N(CH_3)_2OH=$$



Si l'on emploie au lieu du trichlorure de benzényle la benzaldéhyde on arrive d'abord aux leuco dérivés II:

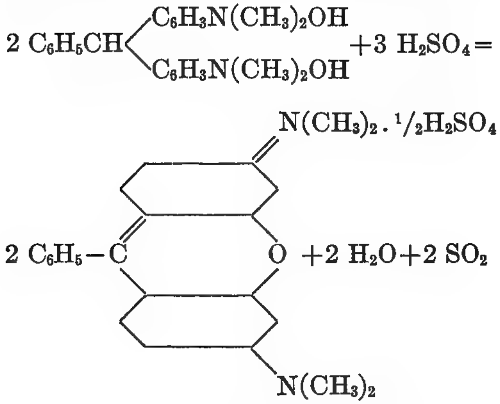


$$C_6H_5CHO\begin{matrix} HC_6H_3N(CH_3)_2OH \\ HC_6H_3N(CH_3)_2OH \end{matrix} = C_6H_5CH\begin{matrix} C_6H_3N(CH_3)_2OH \\ C_6H_3N(CH_3)_2OH \end{matrix}$$

II

Pour effectuer cette condensation, on chauffe la solution alcoolique du m-diaminophénol alcoylé et de la benzaldéhyde avec l'acide sulfurique étendu pendant plusieures heures au bain-marie. Pour arriver à la matière colorante à partir de ces leucoderivés II, il suffit généralement de les chauffer avec l'acide sulfurique concentré à 100° pendant plusieures heures.

La rosamine se forme alors suivant le schème:



Bien qu'on connaisse déjà un certain nombre de ces colorants décrits dans les brevets allemands (D. R. P. Nr. 62 574 et Nr. 150440 de la maison Bayer & Co.), les études scientifiques entreprises à ce subjet se bornent jusqu'ici seulement à deux représentants; ce sont d'une part les recherches de *Biehringer* (Journ. f. prakt. Chemie 54, 256) sur la rosamine dérivée de la benzaldéhyde, et d'autre part celles de *Liebermann* (Berl. Berichte 36,2929 et 37,203), qui avait étudié la rosamine dérivée de l'aldéhyde protocatéchique.

Nous nous sommes proposé de reprendre de plus près l'étude de ces colorants, et nous avons commencé par préparer les trois oxy- et les trois méthoxy-rosamines isomériques en partant des oxybenzaldéhydes et de leur dérivés méthylés correspondants.

La condensation du diméthyl-m-aminophénol avec les oxybenzaldéhydes s'effectue assez facilement et nous avons réussi à obtenir tous les leucodérivés analogues à l'état cristallin.

Toutefois, si l'on soumet ces leucodérivés à l'action de l'acide sulfurique concentré pour les déhydrater et les oxyder, on peut observer, que les substances préparées avec la para et o-oxybenzaldéhyde ainsi que leurs dérivés alcoylés sont beaucoup plus facilement oxydables que celles, obtenues avec les dérivés m-oxy-isomériques, de sorte qu'en chauffant les dérivés para et ortho avec l'acide sulfurique concentré au bain-marie pendant plusieurs heures on arrive à des matières colorantes, tandis qu'avec l'isomère méta on n'obtient que des leucodérivés déshydratés— Ayant aussi préparé les rosamines de *Biehringer* et de *Liebermann*, nous avons eu l'occasion de confirmer l'observation de *Liebermann*, suivant laquelle le produit de condensation du diméthyl-amino-phénol et l'aldéhyde protocatéchique (la dioxy-rosamine) s'oxyde bien plus facilement par l'acide sulfurique concentré que la rosamine de *Biehringer* mentionnée ci-dessus.

D'après *Biehringer* et *Liebermann*, les rosamines obtenues en deshydratant les leucodérivés sans, ou avec oxydation simultanée, au moyen de l'acide sulfurique concentré, devait posséder un groupe SO_3H—dans le noyau benzénique de l'aldéhyde primitive. En effectuant la déshydratation de nos produits cités plus haut, nous avons procédé de la même manière que ces deux chimistes, mais ayant précipité les rosamines de la solution dans l'acide sulfurique par addition d'une solution de chlorure de zinc, nous avons obtenu les colorants respectifs à l'état cristallin, qui constituaient des sels doubles avec le $ZnCl_2$ et dans lesquelles nous n'avons pu constater la présence de groupes SO_3H.

Ces matières colorantes teignent bien la soie en rouge avec une légère fluorescence et le coton mordancé au tanin, mais elles ne se fixent que très faiblement au moyen des mordants de fer et ceux d'alumine.

(Résumé)

SUR LE DOSAGE DE LA PHLOROGLUCINE

EMIL VOTOCEK ET R. POTMESEL

Laboratoire de chimie organique à l'Ecole polytechnique tchèque de Prague, Bohême

1.) On peut doser la phloroglucine en la précipitant de sa solution aqueuse, contentant au moins 2% de HCl, par l'addition d'un excès de furfurol. On pèse la furfurolphloroglucide obtenue.

2.) Les colorants de la série flavonique (apigénine, quercétine, maclurine et morine) ainsi que la phlorétine se laissent dédoubler par l'action de la potasse caustique presque quantitativement avec mise en liberté de 1 molécule de phloroglucine. Ce fait pourra être utilisé dans l'étude des matières colorantes d'origine végétale.

3.) La réaction avec le furfurol en présence d'acide chlorhydrique peut servir à distinguer différents phénols.

ON KOJI ACID, A NEW ORGANIC ACID FORMED BY ASPERGILLUS ORYZAE

Teijiro Yabuta

College of Agriculture, Imperial University, Tokyo

Dr. K. Saito[1] has recently isolated a new organic acid from Aspergillus oryzae, which was grown on steamed rice. For this purpose he has extracted the finely powdered fungus mass with hot water, evaporated the extract to a syrup, which was repeatedly shaken with ether. On evaporating the ethereal solution he has obtained the crude acid, which was purified by recrystallization from hot water. It forms colorless needles giving a strong red coloration with ferric chloride. The qualitative tests have shown that this acid is not identical with oxalic, succinic, citric, malic, tartaric or benzoic acid, which usually occur in the lower fungi. Judging from the melting point and from the characteristic reaction with ferric chloride, he supposed it to be identical with B-resorcyl-carbonic acid. But owing to the difficulty of obtaining the pure acid in large quantities, he did not investigate it any further, so I have tried to clear up the chemical nature of this acid. For this purpose I have prepared fairly large quantities of it in probably a pure state and found the empirical formula to be $C_{12}H_{14}O_8$. From the copper salt, as well as from the acetyl and bezoyl derivatives, the presence of two carboxyl and four hydroxyl groups in the molecule has also been ascertained, so that the formula may be written as $C_{10}H_8(OH_4)(COOH)_2$. It is therefore quite different from B-resorcyl-carbonic acid and so far as I know, the occurrence of such an acid in fungi has never been mentioned before. I have given the name "Koji acid" to this substance.

ISOLATION OF KOJI ACID

For the isolation of koji acid in large quantities I have modified Dr. Saito's method in the following way:

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[1] K. Sgito: The Botanical Magazine (Tokyo), Vol. XXI, No. 249

1.) 150 g steamed rice are put in an Erlenmeyer flask of 500 cc. capacity, which is provided with a cotton air-filter, and after repeated sterilization in Koch's steam sterilizer, it is inoculated with the spores of Aspergillus oryzae and kept at 30–35° for 2–3 weeks, shaking it from time to time. When the rice is fully covered with the mycelium and brown spores of the fungus, it is dried at a low temperature, finely powdered, and extracted with ether in a large Sochlet extraction apparatus. During the extraction a part of the koji acid crystallizes out as colorless needles from the ethereal solution, while a part remains in the solution. The ethereal solution is now evaporated to dryness, and treated with petroleum ether to remove the fatty matter. The crude acid thus obtained is dissolved in a little hot water, decolorized with animal charcoal (which should be free from traces of iron) and evaporated. About 50 g koji acid can be thus obtained from 15 kilo. rice.

2.) Finely powdered koji is extracted with boiling alcohol. The alcoholic extract is evaporated under reduced pressure nearly to dryness. The residue is dissolved in water and precipitated with basic lead acetate, avoiding an excess. The precipitate thus produced is filtered off and the filtrate therefrom is treated with sulphuretted hydrogen to remove the excess of lead and evaporated in vacuum to expel the sulphuretted hydrogen. The acid solution thus obtained is neutralized with caustic soda. By adding a copper sulphate solution to it, the light green copper salt of koji acid is precipitated at once, which is washed with water and decomposed with sulphuretted hydrogen. The filtrate from the copper sulphide which contains the free koji acid is evaporated to a small volume. After cooling the acid separates as colorless needles which may be purified by recrystallization.

The free acid crystallizes in colorless needles or prisms with no water of crystallization. It melts at 152° (not corr.) to a brownish liquid. The crystals have a bitter taste, while the aqueous solution is somewhat sour. The purified acid is rather stable in the air. It is readily soluble in ethyl alcohol, methyl alcohol, water and acetone, less easily in pyridin, slightly in ether and chloroform, and quite insoluble in petroleum ether, ligroin, benzene and carbon tetrachloride. The aqueous solution has an acid reaction to congo-red, phenolphthalein, rosolic acid, litmus and methyl orange. It expels carbonic acid gas from an alkaline carbonate or bicarbonate solution. The aqueous solution gives a strong wine red coloration with ferric chloride, which may be recognized even in the dilution of 1/200,000. No reaction is, however, obtained with ferrous salts. The red coloration disappears on addition of diluted mineral acids and reappears by neutralization. As already mentioned, koji acid is precipitated from its aqueous solution by copper acetate or sulphate, the precipitation being complete, when the solution is previously neutralized with dilute alkali. The acid is not precipitated from it aqueous solution by aqueous or ammoniacal silver nitrate, neutral, basic or ammoniacal lead acetate, tannin, mercuric chloride, phosphotungstic or phosphomolybdic acid. It has no reaction upon alkaline diazobenzosulphonic acid, Nessler's reagent, Millon's reagent, or Fehling's solution. The aqueous solution of the acid absorbs much bromine. Neither methoxyl nor ethoxyl group is recognized by Zeissel's method. When potassium permanganate is added to the alkaline or alkali carbonate solution of koji acid, the latter is oxidized, oxalic acid being one of the oxidation products.

Koji acid leaves no ash after ignition; it contains no nitrogen, sulphur, phosphorus or halogen in its molecule.

Different samples of the acid, purified from various solvents, such as water, alcohol, acetone and ether, were dried in vacuum at 100°, and analysed with the following results:

1.	0.1770 g	subst.	gave	0.3264 g CO_2	0.0776 g H_2O
2.	0.1810 g	“	“	0.3340 g “	0.0840 g “
3.	0.1374 g	“	“	0.2542 g “	0.0626 g “
4.	0.2240 g	“	“	0.4132 g “	0.1000 g “

		%C	%H	%O
$C_{12}H_{14}O_8$ calc.		50.35	4.90	44.45
Found	1.	50.29	4.87	44.84
	2.	50.33	5.15	44.52
	3.	50.49	5.06	44.45
	4.	50.31	4.96	44.73

THE COPPER SALT

The copper salt is easily obtained by adding copper acetate or copper sulphate to the aqueous solution of the acid, which is previously neutralized with caustic soda. The precipitate is collected on a filter and washed with hot water, until the filtrate gives no reaction for sulphuric acid.

The copper salt forms light green rhombic crystals, containing no water of crystallization. It is insoluble in water, alcohol, ether, benzene, petroleum ether and ligroin, but soluble in dilute mineral acids as well as in acetic acid. It dissolves also in dilute ammonia with blue coloration.

The analysis of the salt dried in vacuum at 100° gave the following result:—

1.	0.1179 g subst. gave	0.1782 g CO_2	0.0395 g H_2O
2.	0.1085 g " "	0.1644 g "	0.0365 g "
1.	0.5000 g subst. gave	0.1160 g CuO	
2.	0.7824 g " "	0.1782 g "	

		%C	%H	%O	%Cu
$C_{12}H_{12}O_8Cu$. calc.		41.42	3.45	36.81	18.32
Found	1.	41.22	3.73		18.49
	2.	41.32	3.68		18.19

THE ACETYL DERIVATIVE

1.) The acetyl derivative is obtained by boiling the acid with five times its weight of acetic anhydride in a flask connected with reverted cooler. After heating for 2 hours, it is evaporated under diminished pressure to remove the excess of acetic anhydride and the acetic acid formed by the reaction. The residue is recrystallized several times from hot alcohol.

2.) In the previous method acetic anhydride may be mixed with half of its weight of anhydrous sodium acetate. The acetylated product can be easily separated from sodium acetate by means of ethyl acetate, owing to their different solubilities.

3.) One part of the acid and two parts of acetylchloride are put into a flask, provided with reverted cooler, and gently warmed on the water bath. The reaction takes place very violently with the evolution of hydrochloric acid gas. When the reaction is over, it is evaporated in vacuum to remove the excess of acetyl chloride and hydrochloric acid, and the residue is purified as mentioned above.

The acetyl compound crystallizes from hot alcoholic solution as colorless needles, which melt at 102° to a brownish liquid. It is easily soluble in ethyl acetate, somewhat less in alcohol, and only sparingly in cold water. It dissolves, however, readily in hot water. The acetyl compound has a slightly acid reaction. It gives no precipitate with copper acetate, nor does it show any reaction with ferric chloride, but the above reactions are obtained when it is previously saponified with caustic alkali and neutralized with hydrochloric acid.

Analysis of the acetyl compound, dried in vacuum at 80° gave the following result:—

1.	0.1051 g subst. gave	0.2030 g CO_2	0.0465 g H_2O
2.	0.1234 g " "	0.2386 g CO_2	0.0552 g "

		%C	%H	%O
$C_{12}H_{10}O_4(O.CH_3CO)_4$. calc.........		52.86	4.84	42.30
Found........................	1.	52.67	4.92	42.41
	2.	52.77	4.97	42.26

To give further evidence that the acetyl compound has four acetyl radicals in one molecule, I have determined the acetyl value in the following way:

Into 2 Erlenmeyer's flasks (A and B) were put 1 g each of the sample and after dissolving in 50 c.c. water, one flask (A) was directly titrated with standard caustic soda solution, while the other flask (B) was previously saponified by adding 100 c.c. of standard caustic-soda solution. After keeping for 48 hours at room temperature just so much standard sulphuric acid was added as to neutralize 100 c.c. caustic soda and then titrated with standard soda solution. The difference between the two titrations (A and B) expresses the quantity of standard soda solution, which was used to neutralize the acetic acid produced by the saponification of the acetyl compound. Thus I found:

		Sample used	Before saponification (A)	NaOH used after saponification (B)	Difference
$C_{10}H_8(CO_2H)_2(O.CH_3CO)_4$	calc.	1.000	22.04	66.18	44.14
Found...............	1.	1.000	22.00	66.50	44.50
	2.	1.000	22.00	67.00	45.00

From these observations, it is very probable that the original acid has four hydroxyl groups in one molecule.

THE BENZOYL DERIVATIVES

Two benzoyl derivatives, namely di- and tetra-benzoate corresponding to the formulas $C_{12}H_{10}O_4(OH)_2(OC_6H_5CO)_2$ and $C_{12}H_{10}O_4(OC_6H_5CO)_4$ respectively were obtained in the following way.

1.) Di-benzoyl derivative.

1 g finely powdered koji acid is suspended in 40 c.c. absolute ether, 10 c.c. benzoyl chloride is added to it, and heated in a flask, connected with reverted cooler, for 2–3 hours. After cooling, the reaction product is collected on a filter and washed with petroleum ether to remove the adhering benzoyl chloride. The residue is then dissolved in a little alcohol. On addition of large quantities of cold water, the benzoyl compound separates at once as colorless needles, which may be further purified by repeating the same process.

The benzoyl compound melts at 137° to a brownish liquid. It dissolves only sparingly in cold water, but more easily in hot water. The solubility in alcohol is greater than in water. In ether it is slightly soluble. The benzoyl compound has scarcely an acid reaction. It gives no reaction with copper acetate or with ferric chloride. After saponifying, however, it gives the above reaction.

Analysis of the benzoyl compound, dried in vacuum at 100° gave the following result:

1.	0.1256 g subst. gave	0.2874 g CO_2	0.0530 g H_2O
2.	0.0862 g " "	0.1994 g "	0.0370 g "

		%C	%H	%O
$C_{12}H_{10}O_4(OH)_2(O.C_6H_5CO)_2$ calc.		63.15	4.45	32.40
Found	1.	63.13	4.69	32.18
	2.	63.08	4.76	32.16

2.) Tetra-benzoyl derivative.

1. g koji acid dissolved in 50 c.c. water, is shaken with 10 c.c. benzoyl chloride and 50 c.c. caustic soda solution (15%), cooling with cold water, until the odour of benzoyl chloride vanishes. The benzoyl derivative separating from the solution is collected on a filter, washed with water and recrystallized from hot alcohol which was slightly acidified with hydrochloric acid. The crystals thus obtained are treated with water until the filtrate gives no reaction for chlorine. For further purification, they are repeatedly recrystallized from hot alcohol.

The benzoyl derivative forms colorless plates which melt at 135°. It is very difficultly soluble in water but readily in alcohol or glacial acetic acid.

Analysis of the benzoyl derivative, dried in vacuum at 100° gave the following result:

0.1412 g subst. gave 0.3530 g CO_2 0.0526 H_2O

	%C	%H	%O
$C_{12}H_{10}O_4(O.C_6H_5CO)_4$ calc.	68.37	4.28	27.35
Found	68.23	6.14	27.63

Different varieties of Aspergillus oryzae seem to produce different amounts of koji acid under the same conditions. According to my observation, the varieties isolated from "Tamari-koji" produce more acid than those isolated from "Shoyu" or "Sake-koji." Generally those varieties which liquefy gelatine more powerfully seem to produce more acid.

The acid is also produced by some other aspergillus species, but not by penicillium or mucor, as the following table shows:

Asp.	oryzae	+	Asp.	melleus	—
"	albus	+	"	minimus	—
"	candidus	+	"	fumigatus	—
"	okazakii	—	"	wenti	—

Asp.	niger	—	Mucor	racemosus	—
"	ochraceus	—	"	circineloides	—
"	glaucus	—	"	spinosus	—
"	luchuensis	—	"	mucedo	—
"	nidulans	+	"	stolonifer	—
"	flavus	—	Oidium	lactis	—
"	clavatus	—	Botolytis	cineria	—
"	gigantius	—	Dematium	pullulans	—
"	varians	—	Monilia	candida	—
Penicillium	glaucum	—	"	javanica	—
"	glaurosum	—	"	variabilis	—
"	olivaceum	—	Chalara	mycoderma	—
Mucor	amylomyces	—			

As the acid is also produced by the aspergillus when cultured in "koji-extract," it is easily detected by previously adding a few drops of ferric chloride to the culture medium.

Different culture media behave also differently upon, the production of this acid. Thus, the latter is produced when the aspergillus has grown on certain cereals, such as maize, wheat, barley, rye, oats and italian millet, but not on leguminous seeds as peas, beans, horse beans, broad beans, soja beans, Indian beans, black beans, quaial beans, etc. Among many root crops examined, sweet potato was the only one which produces this acid.

The antiseptic power of koji acid upon mould fungi and yeasts seems to be very weak, as Dr. Saito has already reported. Certain fungi can even assimilate it as a nutriment. But the bacterial growth is generally stopped, when the nutritive medium contains more than 0.5% of this acid.

QUINONOID ADDITION AS THE MECHANISM OF DYESTUFF FORMATION

ARTHUR G. GREEN
The University, Leeds, England

In 1899 Thiele (Ann. 1899, *306*, 132) advanced an explanation of the capacity for addition exhibited by quinones and quinonoid compounds. This explanation he based upon his theory of unsaturation and the existence in such compounds of a chain of conjugate double linkings, attributing to this cause a large number of the reactions which occur with quinonoid dyestuffs. Bucherer in 1907 (Ber. *40*, 3412) further elaborated this hypothesis and referred to a single type all the reactions by which the dyestuffs of the azine, thiazine and oxazine series are produced (cf. Möhlau & Bucherer, "Farbenchemisches Praktikum"). For the past seven or eight years I have been in the habit of employing in my lectures a similar generalisation, though in a somewhat more comprehensive form, which I have found to supply a ready explanation for the formation of complex dyestuff molecules not only of the above classes but also in other groups, e. g., the rosaniline group, for which substitutive reactions are usually assumed.

In view of the great assistance which these generalisations give to the understanding of dyestuff chemistry and the small attention which they have hitherto claimed, I have thought it desirable to supplement the above publications by a description of the form in which I employ this hypothesis. This is, shortly stated, as follows:

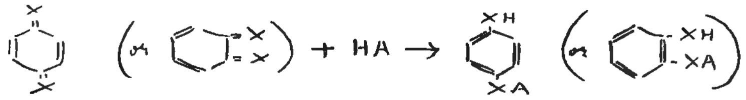
1. All quinones and quinone-like compounds, by reason of their high degree of "unsaturation," exhibit a great attraction for hydrogen or equivalent groups, by the assumption of which they can pass into more saturated compounds.

2. A very large proportion of dyestuff syntheses and the individual steps in such syntheses may be represented as con-

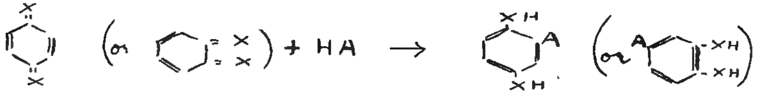
sisting in the linking up of molecules ("Verkettungen") brought about through the attractive forces of quinonoid groups.

3. Such reactions may occur in two ways, viz:—

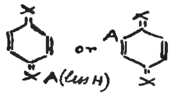
a. Direct Addition:



b. Indirect Addition:



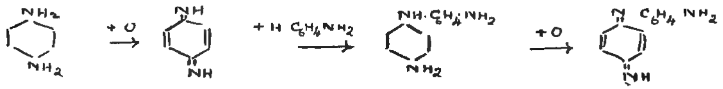
4. In the presence of an oxidising agent such as chromic acid, a chlorate, atmospheric oxygen, or another quinonoid compound, the above addition products are again converted into quinonoid derivatives,



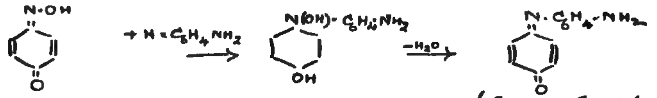
which under suitable conditions are ready to react again in the same way, with production of compounds of still greater complexity. Such alternate additions and reoxidations may occur several times in succession thus producing (as in the Aniline Black and Induline series) very complex molecular structures.

DIRECT QUINONOID ADDITION

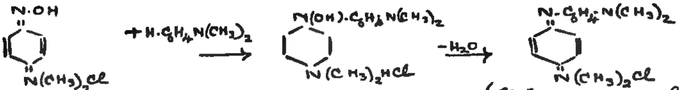
Simple examples of reactions of this type are seen in the formation of the indamines and indophenols by conjoint oxidation of paradiamines or paraamidophenols with amines or phenols. Taking Phenylene Blue as typical of these compounds, the reactions occurring may be represented as follows:—



The formation of indamines or indophenols from nitrosoamines or nitrosophenols can also be represented in a similar manner:

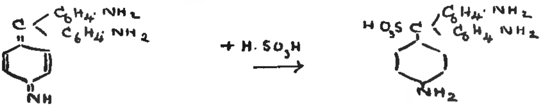


(Simplest Indophenol)

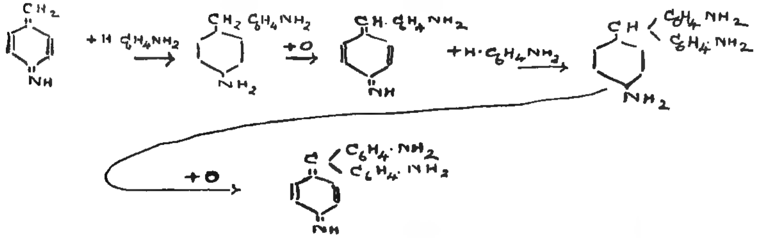


(Bindschedler's Green)

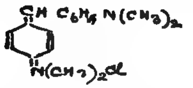
The tendency of the triphenylmethane dyestuffs to form colourless compounds by combination with sulphurous acid, hydric cyanide, water, etc. has been represented by Thiele as follows:—



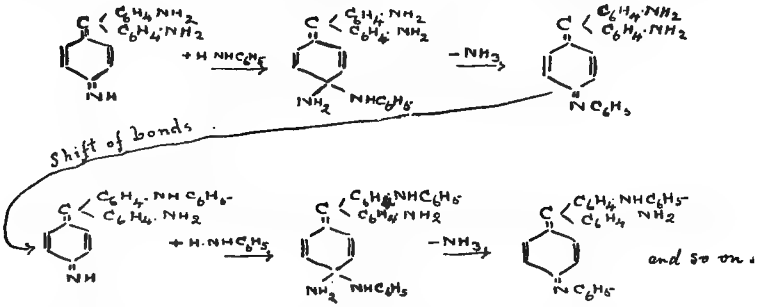
Most of the reactions which lead to the dyestuffs of the triphenylmethane group are in my opinion better explained as addition processes than by the ordinary method of representation. Thus the formation of pararosaniline by oxidation of a mixture of paratoluidine and aniline may be represented by assuming that the former is first oxidised to the carboquinonimide which then reacts with aniline in the following manner:—



The hydrol and phosgene syntheses of triphenylmethane dyestuffs may also be regarded in a similar light. Thus the extraordinary facility with which tetramethyldiamidobenzhydrol undergoes condensation with a wide range of substances is explained if we regard these reactions as due to the additive capacity of the hydrol salt in its quinonoid form:

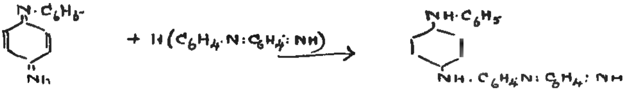


Even the phenylation of rosaniline in the production of Aniline Blue may be regarded with great probability as a quinonoid reaction, though of a different type to the above:



This accounts for the readiness with which phenylation takes place compared with the ordinary phenylation of amines, and also explains the functions of the benzoic acid used. This weak acid preserves a sufficient degree of acidity to determine the splitting off of ammonia without retaining the latter in the reacting mixture, so that the reaction can proceed to completion. If hydrochloric acid is used instead, the accumulation of ammonium chloride brings about an equilibrium, through the reversal of the reaction, when only the moon or diphenylated stage has been reached.

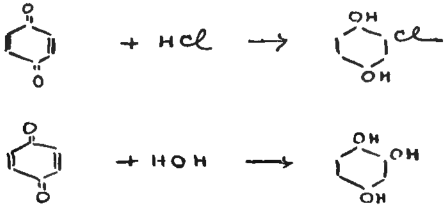
Recent investigations upon Aniline Black have demonstrated that the intermediate products of its formation, emeraldine and nigraniline, are complex indamines containing eight aniline residues linked together in para position. A study of the formation of these compounds (Willstätter & Moore, Ber. *40*, 1907, 2665; Green & Woodhead, Chem. Soc. Trans. *97*, 1910, 2388) makes it very probable that the mechanism of their formation is as follows:—The first oxidation product of aniline capable of isolation is the yellow phenylquinonimide of Caro. This body when treated with mineral acids is at once converted into the blue imide of Willstätter, a reaction which consists in the direct addition of one molecule of the yellow imide to the quinonoid groups of the second:—



Further oxidation of the blue imide gives the red imide of Willstätter, $C_6H_5.N:C_6H_4:N.C_6H_4.N:C_6H_4:NH$, and this also under the influence of mineral acids undergoes a similar addition and produces nigraniline, $C_6H_5.NH.C_6H_4.NH.C_6H_4.N:C_6H_4:N.C_6H_4.N:C_6H_4:N.C_6H_4.N:C_6H_4:NH$. Or the blue imide may, by further self-addition, produce protoemeraldine, $C_6H_5.NH.C_6H_4.NH.C_6H_4.NH.C_6H_4.NH.C_6H_4.NH.C_6H_4.NH.C_6H_4.N:C_6H_4:NH$, which latter body upon oxidation gives emeraldine and nigraniline. The tendency to the formation of such complex molecules is thus readily explained.

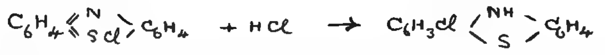
INDIRECT QUINONOID ADDITION

Simple examples of indirect quinonoid addition are to be found in the convertion of quinone into chloro- or hydroxy- hydroquinone by the action of hydrochloric acid or of caustic soda respectively (Barth & Schreder, Ber. *12*, 417, 503):—



An important case in which the latter reaction occurs is the formation of dioxyanthraquinone (alizarine) by caustic soda fusion of anthraquinone monosulphonic acid or even of anthraquinone itself, and a similar introduction of hydroxyl probably constitutes an intermediate stage in the production of Indanthrene Blue by the alkaline fusion of betaamidoanthraquinone. Thiele (Ber. *31*, 1898, 1247; Ann. 1900, *311*, 341) has also found that acetyl derivatives of chloro- or hydroxy-hydroquinone are readily formed from benzoquinone by the action of zinc chloride or concentrated sulphuric acid respectively in presence of acetic anhydride. A similar reaction has been described by Schultz (Ber. *15*, 1882, 652) who obtained diacetyldichlorohydroquinone by the action of acetyl chloride on quinone.

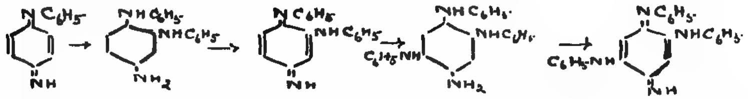
Many analogous cases have been observed amongst orthoquinonoid dyestuffs, thus Page & Smiles (Chem. Soc. Trans. *97*, 1910, 1112) have observed the ready formation of chloro compounds from phenazthionium salts when heated with hydrochloric acid:



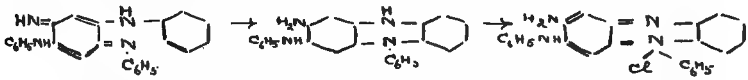
$$C_6H_4\left\langle\begin{matrix}N\\SCl\end{matrix}\right\rangle C_6H_4 + HCl \rightarrow C_6H_3Cl\left\langle\begin{matrix}NH\\S\end{matrix}\right\rangle C_6H_4$$

Other simple cases of indirect quinonoid addition are to be found in the formation of paraphynylenediamine sulphonic acid, and of the mono- di- and tetra-thiosulphonic acids of paraphenylenediamine obtained by oxidation of this base in presence of sulphurous or thiosulphuric acids (cf. Green & Perkin, Trans. Chem. Soc. *83*, 1903, 1201). Probably similar reactions, giving rise to intermediate SH compounds, constitute an important factor in the formation of sulphur dyestuffs when paraamidophenols and oxydiphenylamine derivatives are heated with sodium polysulphide.

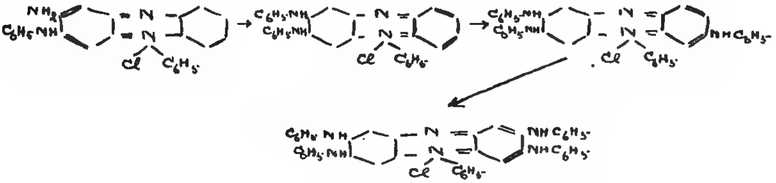
The direct introduction of amido groups or amine residues into the nucleus of quinones or quinonoid compounds is known in a large number of cases. Thus alpha and betanaphthoquinones treated with aniline are readily converted into their monoanilido derivatives, $C_{10}H_5O_2(NHC_6H_5)$; whilst benzoquinone gives the dianilidobenzoquinone and its anilides. Anilido derivatives of benzoquinone and of benzoquinoneanilides are also produced when aniline is subjected to oxidation under neutral or very feebly acid conditions (cf. Willstätter & Majima Ber. *43*, 1910, 2588; Majima Ber. *44*, 1911, 229, 3080). These compounds constitute the intermediate stages in the formation of indulines and nigrosines in which cases the role of oxidising agent is fulfilled by the amidoazobenzene or nitrobenzene respectively. Assuming as before that the primary oxidation product of aniline is again the yellow imide of Caro, we may picture the further condensation to occur by alternate addition and reoxidation in the following manner:—



All these compounds give rise to indulines upon heating with aniline and aniline hydrochloride, the closing of the phenazonium ring being attributable to direct quinonoid addition, in which the amine residue taking part in the reaction is a portion of the quinonoid molecule itself:



By the transference of the quinonoid bonds to the other ring, an occurrence which has been specially studied by Kehrmann (Ber. *31*, 977) this ring also becomes capable of indirect attention and thus a further introduction of amine residues is effected and bluer shades of induline produced.

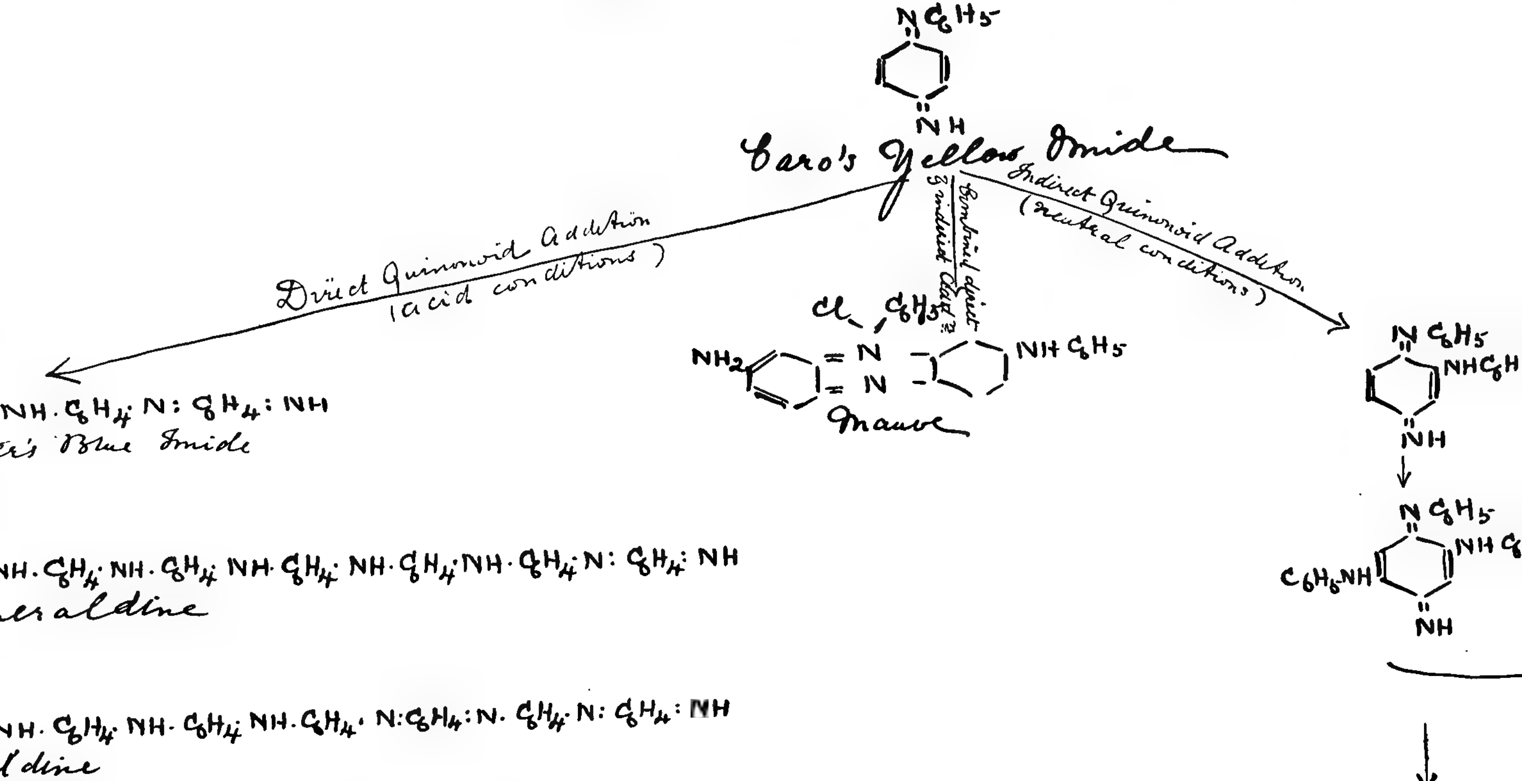


The introduction of amine residues into the benzene or naphthalene nucleus, brought about by indirect quinonoid addition, has been observed in a large number of cases in the azine thiazine and oxazine series. Amongst them may be instanced the conversion of phenylphenazonium chloride into aposafranine, of phenylnaphthophenazonium chloride into rosinduline, and of Meldola's Blue into substituted derivatives of Nile Blue.

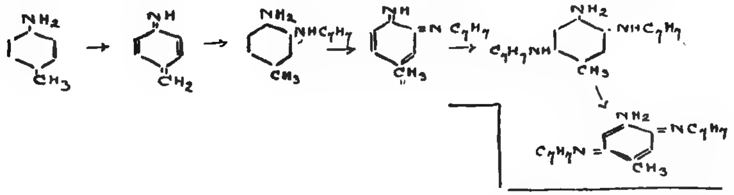
The formation of all dyestuffs belonging to the azine, oxazine, and thiazine series, starting from their respective raw materials, are readily represented by a series of indirect and direct quinonoid additions with intermediate reoxidations (cf. Bucherer).

Similar considerations can probably be applied to explain the formation of other classes of dyestuffs. Thus the great tendency exhibited in the anthraquinone series to the production

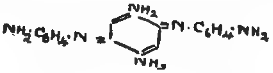
Scheme for Oxidation of Aniline



NC6H5
NH
Caro's Yellow Imide
Direct Quinonoid Addition (acid conditions)
Combined direct & indirect Add?
Indirect Quinonoid Addition (neutral conditions)
NH.C6H4:N:C6H4:NH
er's Blue Imide
NH.C6H4.NH.C6H4.NH.C6H4.NH.C6H4.NH.C6H4.N:C6H4:NH
eraldine
NH.C6H4.NH.C6H4.NH.C6H4.N:C6H4:N.C6H4.N:C6H4:NH
ldine
Cl C6H5
NH2
N
N
NH C6H5
Mauve
N C6H5
NHC6H
NH
N C6H5
NH C6
C6H5NH
NH



The production of Bandrowski's base, from paraphenylenediamine may be attributed to an analogous reaction starting from quinone diimide.



(*Abstract*)

COAL-TAR COLORS AND INJURY TO HEALTH

E. E. Smith
New York, N. Y.

Difficulty exists in deciding the question of harmlessness of colors because all substances, including food, are capable of producing injurious effects if ingested in sufficient amount; that is, the question is a quantitative one. The injurious action may arise because the quantity ingested exceeds the capacity of physiological adaptation. Hence, because a certain large quantity of color, when administered to an animal, produces a harmful effect, it may not be concluded that the color is essentially injurious. Such an observation establishes the quality of action; whether it is essentially injurious will be determined by whether the amount in food is or is not removed by a wide margin of safety from the quantity capable of producing the observed quality of action. The extent of such a margin that is necessary varies with the particular quality of action.

In determining the matter of quantity, a numerical expression of how much of a given color per given weight of animal would produce injurious effect cannot be obtained, because the production of injury varies with the species of animal, the individual of the same species, the size and age of the animal and with the particular quality of action. Hence, while the quality of action may be determined by animal experiments, the quantitative relation must be determined by observations on humans. Actual injury need not be produced. It is only necessary to demonstrate a wide margin of safety.

In the selection of the seven permitted colors F. I. D. 76, the procedure of eliminating from consideration those colors which are described in literature to have produced unfavorable effects is an evasion rather than a rational interpretation of the facts since it has merely led to the adoption of colors six of which have been inadequately investigated. It is not questioned that their selection is fully justified on other grounds.

(*Abstract*)

THE NEED OF OFFICIAL TESTS IN DYEING AND TEXTILE CHEMISTRY

L. DaCosta Ward
Philadelphia Textile School, Philadelphia, Pa.

The writer calls attention to the lack of uniformity in the testing of dyestuffs for fastness to various agencies, and in other lines of textile chemistry.

The opinion is expressed that the class, *i.e.*, acid, basic, substantive, etc., is irrelevant to the question of fastness and that a dyestuff called "fast," for instance, should fulfil or pass certain official or standard tests, depending upon the agent to which reference is made.

Co-operation is urged of the various dyers' societies with the color manufacturers with the object of establishing a uniform system of color testing, and of textile chemists among themselves and if necessary with the textile manufacturers' associations in standardizing methods at present employed.

USE AND DETECTION OF COLORING MATTERS IN FOODS

Harvey W. Wiley and Aida M. Doyle
Washington, D. C.

This paper has been prepared by its authors in the hope that a few years will see no necessity for the further practice of the chemical methods for the detection of colors in foods, herein described. Increasing knowledge of the use of food colors, and a study of their purpose and effects, convinces me more and more that the artificial coloring of food is an ethical, moral, and dietetic sin, and should be rigidly prohibited by Municipal, State and Federal laws, but this ideal condition has not yet been attained and therefore, a systematic and scientific scheme, by which the chemist can detect these artificial colors, classify them, and thus lay the foundation for further work of a prohibitory kind is most useful.

FABRICATION D'UNE FARINE SUCRÉE DE BETTERAVE "BEETMEAL" SON EMPLOI DANS L'ALIMENTATION HUMAINE ET ANIMALE

A. Aulard
Bruxelles, Belgium

Au précédent Congrès international de chimie appliquée, Londres 1909, je fis une communication sur la fabrication d'une farine végétale sucrée en utilisant la betterave comme matière première.

Depuis cette communication, une usine, celle de Daussoulx Vedrin (Belgique) va commencer sa troisième fabrication et, jusqu'à ce jour, toute sa production s'est enlevée en quelques semaines; aussi dès la campagne prochaine 1912, une seconde usine entrera-t-elle en fonctionnement, en France, près de Dunkerque et la Société Civile Belge des brevets Dautrebande (brevets accordés en Allemagne, pays pourtant si difficile dans l'octroi de ses brevets qui acquièrent ainsi une valeur réelle) songe à créer diverses grosses usines susceptibles de traiter chacune annuellement de 30 à 50,000 tonnes de betteraves. C'est vous dire, Messieurs, qu'une industrie nouvelle, la farine de betterave, baptisée à son début "Beetmeal" a vu le jour sur ce petit coin de terre si fertile qu'est l'industrieuse Belgique.

Cette industrie nouvelle, pour accomplir économiquement la dessiccation de la betterave, avait besoin d'un dessiccateur pratique permettant l'utilisation des gaz perdus des générateurs, ou l'utilisation intégrale des calories provenant de houille mi-grasse ou maigre, brûlée dans un foyer spécial.

Après des essais accomplis avec divers dessiccateurs, la préférence fut donnée au dessiccateur vertical A. Huillard, de Suresnes, qui, seul, permet la dessiccation rationnelle de la betterave à température comprise entre 120° maximum et 40° à la sortie. Je n'entrerai pas dans les détails techniques de l'opération de la dessiccation de la betterave. Il n'est pas aussi aisé qu'on le croirait à première vue, d'extraire l'eau emprisonnée avec le sucre dans une multitude infinie de petites cellules. Le protoplasme des cellules, s'il est chauffé immodérément au début, se contracte et laisse exsuder le jus sucré, ce qui rend le séchage excessivement difficile; il faut donc que la cellule gonfle sans se rompre, ce qui n'est possible que dans le dessiccateur Huillard, à plateaux superposés et à courant rationnel d'air chaud de bas en haut, de plus en plus humide vers la sortie des gaz. Les cossettes de betterave aussi bien sectionnées que possible, sont déversées sur un premier plateau ou elles rencontrent préférablement à une haute température sèche, de la vapeur d'eau mélangée d'air chaud non entièrement saturé, la température sèche coagulant la substance albuminoïde du protoplasme, comme la chose a lieu dans la plupart des dessiccateurs existants. Dans le Huillard, les cellules de la betterave se gonflent et sont aptes à laisser évaporer l'eau qu'elles contiennent; aux plateaux suivants, elles se trouvent dans un intensif et entraînant courant d'air, de moins en moins chargé de vapeur d'eau et conséquemment de plus en plus sec et de plus en plus chaud (120° cent.) au plateau inférieur, en un état hygrométrique de l'air se rapprochant de zéro.

Le sucre dans la cossette sèche que voici, se trouve emprisonné dans la matière végétale susceptible de reprendre sa forme de cossette humide et non à l'extérieur de cellules incapables de se gonfler, de réabsorber de l'eau, parce que desséchées à trop haute température.

Un tel produit est apte à fournir en diffusion un aussi bon travail qu'avec de la cossette fraîche; son épuisement serait progressif et complet en un produit dense et très pur.

Aux Etats-Unis, là ou la main-d'oeuvre coûte très cher, ou les distances sont très grandes, il y aurait lieu de créer des sècheries de betterave qui permettraient aux sucreries existantes de travailler de la cossette sucrée sèche durant toute l'année. La chose est possible aujourd'hui, grâce au dessiccateur très rationnel de M. A. Huillard, qu'on peut adjoindre à des industries existantes, n'ayant pas à utiliser les gaz perdus de leurs carneaux et pouvant les céder à une sècherie adjacente.

Mais revenons au "Beetmeal." Sa composition est la suivante, d'après la moyenne de mes nombreuses analyses, en employant à la dessiccation une bonne betterave sucrière, composition centésimale du Beetmeal:

Matières albuminoïdes azotées	6,60[1]
Saccharose	65,50
Matières hydrocarbonées	12,75[1]
Cellulose saccharifiable	5,20
Matières grasses	0,75
Eau	5,40
Résidus, matières inertes salines	3,80
	100,00

Un tel produit n'est pas à vrai dire un aliment complet; il renferme trop d'hydrates de carbone par rapport aux substances proteïques qui sont en trop faible quantité; toutefois un tel produit indéfiniment conservable (j'en ai conservé sans moisissures pendant trois années) peut entrer dans la composition de tous les tourteaux, arachide, coton, coprach, lin, etc. et des farines de cocotier et autres, trop pauvres en hydrates de carbone et trop riches en protéïne. Il les enrichit en sucre, rendant plus digestible et assimilable les principes digestibles auxquels le "Beetmeal" a communiqué ainsi une plus grande valeur.

Nous ne devons pas oublier que la physiologie expérimentale a établi que les muscles puisent les matériaux nécessaires à l'accomplissement de leurs fonctions dans la riche provision de glycogène qui les irrigue. Si l'alimentation est assez riche en substances hydrocarbonées (sucre), celles-ci sont directement utilisées; dans le cas contraire, ou bien l'animal transforme en hydrates de carbone les graisses et albuminoïdes de sa ration, ou bien il consomme ses réserves, ou encore les deux phénomènes se passent en même temps.

Ces faits bien acquis ont une grande importance; ils conduisent, en effet, à restreindre la proportion des matières azotées de la ration à la quantité indispensable pour la réparation des tissus et des muscles et à augmenter dans une notable proportion, chez l'homme comme chez l'animal, soumis à un travail intensif, la quantité des substances non azotées: amidon, sucre, matières grasses. Pour l'éleveur, ce fait présente un intérêt capital; en effet, *le coût de l'unité de substance azotée dans les fourrages est beaucoup plus élevé que celui de la substance hydrocarbonée* (sucre). Le Beetmeal, farine de betterave à sucre, vient donc bien à son heure apporter sa quote part à l'enrichissement des aliments sains et indispensables à la nourriture de nos bestiaux et de nos chevaux.

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[1] Composés organiques azotés de combinaisons diverses (asparagine, glutamine, leucine, tyrocine, lecithine et diverses matières de nature albuminoïde, des bases, des enzymes, des peptones, etc.); rien n'est plus complexe que la composition des produits végétaux, surtout la betterave sucrière.

D'après les comptes de l'usine de Daussoulx, les 100 Kgs de Beetmeal pourraient être vendus 20 francs, ce qui mettrait l'unité sucre en partant d'un produit à 65% et à 25% de substances nutritives autres, albuminoïdes et azotées, auxquelles je n'attribue qu'une valeur de 15 frs. les 100 Kgs. à $25 \times 15 = 3.75$ frs. à déduire de $20 = 16.25$ frs. les 65 Kgs. de sucre, soit 25 frs. les 100 Kgs., ce qui, en Belgique, en regard du prix du sucre, sans les droits, est de 6 à 7 frs. inférieur au prix du cristallisé. En partant d'une betterave à 30 frs. la tonne rendue usine et en calculant que la dite racine peut donner au minimum 250 Kgs. de Beetmeal, comptés comme extrait sec, il faudra enlever 750 Kgs. d'eau à la tonne de racine qui, en usine utilisant les gaz des carneaux demandera au maximum 90 Kgs. de combustible plus celui nécessaire à la machinerie, environ 30 Kgs., soit 120 Kgs. à 18 frs. la tonne rendue 2,16 frs.

Le coût de la main d'oeuvre ne dépassera pas 3,50 frs. et celui des frais accessoires un franc; soit au total 6,66 frs. à la tonne de betterave. Si on ajoute les frais généraux et divers, on arrivera probablement à 10 frs. de frais totaux (soit quatre francs aux 100 Kgs. de Beetmeal); si on ajoute le prix du produit, 30 frs., on obtient 40 frs. de dépenses pour une recette de 250 Kgs. de Beetmeal à 20 frs. les 100 Kgs., soit 50 frs. Comme moi, Messieurs, vous jugerez qu'il y de la marge et que cette nouvelle industrie mérite d'être prise en très sérieuse considération, aujourd'hui que la Belgique vous montre la voie à suivre; elle le mérite d'autant plus que je faisais ressortir au Congrès de Londres que l'homme, également, pouvait utiliser cette farine très pure à la confection de divers produits sucrés; j'écrivais ce qui suit et qu'il est bon de redire parfois:

"L'emploi de la farine de betterave à sucre peut, en agriculture, se répandre facilement et rapidement surtout en Angleterre; ce n'est pas que le bétail seul qui peut l'utiliser avec grand avantage; en brasserie, en distillerie, (j'ajouterai aujourd'hui en sucrerie) elle aurait son rôle tout indiqué, en ce pays surtout ou l'emploi du sucre en brasserie a pris un merveilleux essor; elle peut également s'employer dans la confection des pains sucrés (3 à 5% de Beetmeal) ainsi que le Président de l'Association des chimistes de sucrerie et de Distillerie de France, Monsieur Dupont, en recommandait la fabrication (pour le pain des troupes et de la marine), tout comme dans vos nombreux cakes et puddings. J'ajouterai qu'en brasserie la farine sucrée de betterave ne communique aucun mauvais goût à la bière et que la drèche dans laquelle se retrouve la pulpe de betterave est notablement bonifiée. Divers brasseurs belges s'en servent avec succès et s'en trouvent fort bien.

Le cadre de cette petite étude est trop restreint pour lui donner plus d'étendue à la question; tout le monde ici connaît le rôle physiologique du sucre dans l'alimentation humaine; aussi terminerai-je la présente communication en vous disant: Par tous les moyens qui sont en votre pouvoir, répandez le sucre dans votre alimentation et dans celle du cheptel de tous les agriculteurs et, pour ce faire, produisez le aussi bon marché que possible à vingt francs les 100 Kgs. comme il peut être produit par la farine de betterave à sucre.

LA DESSICCATION DES PRODUITS VÉGÉTAUX ET DES SOUS PRODUITS INDUSTRIELS S'IMPOSE-T-ELLE?

A. Aulard
Bruxelles, Belgium

Au VII^e Congrès international de Chimie appliquée, qui se tint à Londres en 1909, je fis diverses communications sur la dessiccation des produits végétaux et des produits résiduaires industriels, tels que les pulpes de sucrerie, les drèches de brasserie et de distillerie etc . . . ; tous produits résiduaires trop aqueux, fermentescibles, s'altérant rapidement et profondément à l'air. Je constate avec plaisir que certains pays comme l'Allemagne, Autriche, l'Italie, la Russie se sont mis résolument à la dessiccation, mais avec regret, que trop de pays encore parmi les plus riches et les plus industriels, n'en comprennent pas tous les bienfaits.

C'est aussi de la chimie appliquée et de la bonne que celle-qui consiste à ne pas laisser s'altérer, à ne pas laisser se détruire ce que la nature a créé surtout lorsqu'on le peut économiquement en utilisant les gaz des carneaux à la dessiccation des produits végétaux et résiduaires de sucrerie, distillerie, brasserie etc.; gaz qui sont employés rationnellement et avec plein succés en Italie, en France et en Russie, dans les nombreuses usines qui ont suivi l'impulsion donnée par mes écrits. Ne rien perdre c'est encore créer; c'est apporter sa quote part au bien être général; c'est à quoi tendent tous mes efforts. De nos jours nous perdons encore trop de matiéres nutritives, feuilles de betteraves, de pommes de terre, de chicorées etc . . . , nous gaspillons nos ressources et nos richesses alimentaires en prodigues inconscients; ne dispersons nous par aux quatre vents tout l'or renfermé dans les calories des gaz des carneaux des générateurs dont nos industries se servent?

L'industrie surcrière betteravière mondiale, emploie les précieuses racines sucrées récoltées sur environ 2.150.000 hectares à 25.000 Kgs de récolte en moyenne par hectare; elles travaillent donc annuellement 55.000.000 de tonnes de betteraves. La consommation moyenne en houille, dans les sucreries, s'élève à 90 kgs à la tonne de betteraves, les unes un peu plus les autres un peu moins, soit 4.950.000 tonnes de combustibles, susceptibles de développer en moyenne, en admettant tout charbon à 7.500 calories, 37.125 billions de calories dont le quart sera entraîné aux carneaux et inutilisé; soit 9.281 billions 250 millions de calories qui seraient susceptibles d'évaporer pratiquement (en dessiccateur Huillard, récupérant les gaz chauds) un Kg d'eau par 600 calories perdues, soit 15.468.750 mètres cubes d'eau, ce qui correspond à la fabrication de 185.254.491 Kgs de pulpe sèche à 90% d'extrait sec, c'est à dire à la dessiccation gratuite de toutes les pulpes à provenir de 120.000 hectares de betteraves, les emblavements de la Belgique et de la Hollande réunies.

En calculant le combustible à 17.50 frs. la tonne, rendue à la sucrerie (ce qui est plutôt un minimum qu'un maximum) notre industrie sucrière de betterave, envoie annuellement dans les airs, en l'espace de moins de trois mois, pour 21.656.250 frs. de calories, dont les 85% pourraient être récupérables et utilisés à la dessiccation de la pulpe de diffusion des betteraves; ce produit mis en silos, se détériore rapidement, perd jusqu'à un tiers de sa valeur et peut même nuire, considérablement à la santé des bestiaux qui le consomment, comme l'ont démontre divers expérimentateurs, entre autres M. C. Moussu dans son étude intitulée "*sur les maladies des pulpes.*" Il s'exprime ainsi qu'il suit: "Il a été démontré de façon formelle que les liquides qui s'écoulent des pulpes fermentées et altérées *sont toxiques même après stèrilisation et filtration sur bougie de porcelaine;* rien d'étonnant dès lors *que les pulpes entières deviennent toxiques* après leur absorption digestive."

Je ne reviendrai pas plus longuemet sur ce que j'ai dit à ce sujet au Congrès de Londres et sur ce que je ne cesse de redire depuis longtemps. Il est heureux que les bestiaux ne peuvent protester, sans quoi ils seraient unanimés à nous faire comprendre l'illogisme de notre conduite.

Nous perdons bénévolement, comme de j'ai démontré antérieurement, en hydrates de carbone détruits en calories non utilisées, en transports onéreux et inutiles d'eau, un gros million de francs journellement, ce pour l'industrie sucrière seule; mais que ne perd-t-on pas en distillerie de grains, de betteraves, en brasserie, en amidonnerie etc. . . . usines fonctionnant toute l'année? Croyez-moi, c'est à nous chimistes, qui avons pu nous rendre compte de tous les phénomènes du séchage, de l'excellence de la bonne conservation des produits ayant subit une dessiccation à base température, comme dans les appareils Huillard auxquels vont toutes mes préférences, préférences basées sur la pratique industrielle, ces dessiccateurs utilisant des gaz perdus et les admettant dilués d'air sec à 120° de température pour les rejeter saturés d'eau à 40° cent; c'est à nous, dis-je d'enseigner sans cesse à mieux faire. Une fois de plus j'aurais pu apporter en ce Congrès international de chimie appliquée de nombreuses analyses confirmant mes assertions, mais comme elles n'auraient fait que confirmer les multiples essais de certains de mes collègues mes analyses précédentes et les travaux très judicieux de Büttner sur le séchage en agriculture etc. . . ., j'ai jugé que mieux valait frapper votre esprit par de gros chiffres irréfutables et contrôlables; peut-être vous engageront-ils à unir vos efforts aux miens afin de parvenir à vaincre la routine industrielle et à faire admettre la dessiccation au moins pour les produits végétaux et résidus industriels périssables, quelque soit le mode de dessiccation employé; Alph. Huillard, Büttner et Meyers, Gummer, Mackensen, Impérial de Harzen Werke, Sperber, Petry-Heeking, Säuberlich, Wüstenhagen, Kuthe, Knauer etc.; quels qu'ils soient, ils feront faire un énorme progrès aux industries que nous servons et ne cessons de conseiller; ils coopéreront à l'amélioration de la nouriture de nos bestiaux tout en les bonifiant considérablement. C'est pourquoi, Messieurs, nous pouvons conclure de façon affirmative et répondre que la dessiccation des produits végétaux et des sous-produits industriels *s'impose,* parce qu'elle est hygiénique, économique et rémunératrice.

L'EMPLOI DE LA CELLULOSE (PÂTE À PAPIER) COMME PRODUIT FILTRANT DANS L'INDUSTRIE SUCRIÈRE ET AUTRES

A. Aulard

Bruxelles, Belgium

Pour la filtration des jus et sirops, l'industrie a employé bien des produits depuis le noir animal, qui lui, au moins, avait une action physique bien déterminée; il absorbait une certaine quantité de sels, de matières organiques, et décolorait profondément les jus et sirops. Il est vrai que pour éviter une grosse perte en sucre, le noir lavé au moyen d'une quantité d'eau assez considérable restituait en un produit dilué la presque totalité des sels et matières organiques absorbés. Il fallait concentrer les petits jus de lavage qui constituaient un produit secondaire, d'ou complication que les filtres mécaniques sont venus heureusement supprimer.

Les filtres mécaniques qui eurent comme préconisateur, un Belge très persévérant, Monsieur Oscar Puvrez (1878) furent tous basés sur l'emploi de tissus de coton plus ou moins serrés, plus ou moins spongieux. Aux toiles en chanvre ou en coton qui subsistent toujours, on s'est efforcé de substituer l'éponge, le feutre l'amiante, etc. . . . les filtres à coke, gravier, brique pilée, noir artificiel, laine de bois, crin végétal et divers autres produits et, comme support spongieux enrobant les précipités tenus et facilitant la filtration des produits colloïdaux, le Koiselghur, farine fossile.

Les divers filtres à sable dont je préconisais l'emploi au précédent Congrès international de chimie appliquée qui se tint à Londres, n'ont rien perdu de leur réelle valeur, mais ils ont vu surgir l'emploi d'un produit plus maniable, plus facilement lavable encore que le sable; *la pâte à papier ou cellulose brute.* Il y a longtemps qu'on songeait à employer dans l'industrie le papier à filtrer qui, dans nos laboratoires, sous forme de filtre plissé, nous a toujours donné toute satisfaction et limpidité parfaite, quelle que soit la nature du précipité; mais l'entonnoir servant de support à la matière filtrante, si je puis m'exprimer ainsi, n'était pas encore trouvé. Monsieur H. Périn, administrateur délégué des sucreries-raffinerie de Chalon-sur-Saône (France) s'en est chargé et, depuis que son filtre très pratique et peu encombrant, garni de pâte de cellulose fonctionne, il a su donner au produit sucré une limpidité que la toile ne saurait rendre.

Je ne décrirai pas le filtre Perrin en cette courte étude; j'en ai donné une description complète dans les communications que je fis à la *Société technique et chimique de sucrerie de Belgique*, (mars 1912), dont l'organe est la *Sucrerie Belge* rédigée par notre éminent et savant collègue M. F. Sachs, qui, a regret, ne peut participer à ce Congrès.

Je veux toutefois attirer votre attention, sur les points suivants qui militent en faveur de l'emploi de la pâte de cellulose dans notre industrie (sucrerie, raffinerie, glucoserie, fabrication des liqueurs etc. . . .) Quelle que soit l'excellence de tissage de la toile employée à la filtration mécanique, cette toile est composée de chaînes et de trames; les fils composant la chaîne subissent des manipulations et un encollage qui augmentent leur solidité et facilitent leur glissage; les fils de trame sont traités différement et mouillés; c'est pourquoi, quelque soit le tissu obtenu, l'âme des fils de chaîne n'est pas la même que celle des fils de trame et les tissus ne sauraient être homogènes. Les interstices existent, aussi petits soient-ils et présentent une succession de parties faibles, attendu que les fils de chaîne ne sont que pressés plus ou moins fort les uns contre les autres et maintenus par les fils de trame, tantôt au-dessus, tantôt au-dessous et moins serrés encore les uns contre les autres que les fils de chaîne; c'est pourquoi dans tous début de filtration sur toile, quelle qu'elle soit, chanvre ou coten, le liquide passe toujours trouble durant un temps plus ou moins long, ce qui n'existe pas sur un filtre préparé à la pâte de cellulose. La filtration des jus et sirops se faisant sous la plus faible pression possible, sur une plaque de cellulose de 20 à 50 mm. d'épaisseur, présente en toutes ses parties une homogénéité parfaite; la filtration ne saurait donc donner que des produits absolument limpides, si limpides même qu'une eau bleutée au moyen de bleu d'Outremer très fin, filtrera incolore sur une couche de cellulose de 10 mm. d'épaisseur; cette même eau artificiellement colorée filtrera bleue durant assez longtemps sur filtre garni de toile très serrée en coton et elle demandera une épaisseur de sable de 20 centimé tres pour filtrer incolore et encore, pas dès le début de la filtration comme sur la cellulose.

Le pouvoir filtrant de la cellulose est donc fort grand, comme l'a démontré le Dr. Hazewinkel, dans son remarquable et long rapport sur les essais effectués à Wonopringgo (Java). *Trois carres six dixièmes* de surface filtrante garnie de pâte à papier, remplacèrent *cinq filtres Dehne* qui ordinairement filtrent le jus concentré non sulfité; le débit du filtre Perrin fut de 52 Hect. par heure, soit 1248 hect. de sirop, à plus de 30° Baume en moyenne, par 24 heures de fonctionnement ininterrompu.

C'est là un résultat remarquable que la pratique a confirmé; c'est pourquoi j'appelle votre attention sur l'emploi de la pâte de cellulose pour toutes les filtrations industrielles qui exigent des produits d'une limpidité absolue.

QUELLE QUE SOIT LA TEMPÉRATURE (90 À 150° CENTIGRADES) À LAQUELLE ON SOUMET LES SOLUTIONS DE SACCHAROSE DE GLUCOSE, DE MALTOSE, ETC., PURES OU IMPURES, CES HYDRATES DE CARBONES PEUVENT ILS SE TRANSFORMER EN CARAMEL, OU L'UN DE SES DÉRIVÉS, EN MILIEU HUMIDE À L'ABRI DE L'AIR?

A. Aulard
Bruxelles, Belgium

Le titre du présent mémoire ainsi posé, la solution à lui donner serait simple et laconique; tout chimiste, ignorant les finesses de l'art sucrier et les controverses auxquelles ces finesses donnent lieu, n'hésiterait par à répondre catégoriquement, qu'en milieu humide, sans *déshydratation possible* de la saccharose, aucune formation de caramel ou de ses dérivés ne saurait se créer et que dut-on faire bouillir à 150° durant une heure la saccharose pure en dissolution concentrée, le niveau de la solution restant artificiellement constant, il ne saurait se créer de caramel ni aucun de ses dérivés; se qui plus est, la solution concentrée même à 1330 de densité, resterait parfaitement incolore ou de même coloration qu'avant ébullition et concentration. Il faut une ébullition prolongée *de plusieurs jours* pour que la simple ébullition du sucre dans l'eau donne une certaine inversion de la saccharose; elle est progressive et peut même devenir complète suivant la formule—$C^{12}H^{22}O^{11}+H^{2}O=C^{6}H^{12}O^{6}+C^{6}O^{12}O^{6}$, partie égale de glucose et de lévulose.

Dans l'industrie sucrière on emploie trop souvent le mot caramel pour désigner des substances chromogènes diverses qui peuvent se développer durant les différentes phases et dans certaines conditions défavorables du travail; on ne doit pas oublier qu'en sucrerie plus qu'en raffinerie on opère sur des produits de puretés variables, les impuretés, étant constituées par des sels à base de potasse et de soude et des produits organiques excessivement complexes, produits qui peuvent réagir sur la saccharose et même entre eux, mais qui ne sauraient créer de caramel ou l'un quelconque de ses dérivés dans les conditions d'un travail rationnel.

Au laboratoire des raffineries de Saint Louis à Marseille, il y a nombre d'années déjà sous l'impulsion de M. Maurice Desbief, je me suis livré à de patientes recherches, tant sur les produits de raffinerie que sur ceux des sucreries de Laudun l'Ardoise et d'Orange, au sujet de la formation des produits colorés en cours d'évaporation ou de cuisson des divers produits sucrés; aussi suis-je devenu excessivement sceptique sur la facilité avec laquelle beaucoup de mes honorables collègues découvrent du caramel ou enregistrent des destructions de sucre durant l'évaporation en préévaporateur Kestner, Pauly ou autre. Je suis devenu encore plus incrédule après avoir lu le remarquable travail de M. Jean Krutwig, professeur à l'Université de Liège, qui confirme mes essais particuliers; ce travail est intitulé: "*Sur la cause de la formation des soi-disant matières colorantes dans les jus de sucrerie.* (Premier Congrès internationnal technique et chimique de sucrerie et de distillerie, Liége 5-10 Juillet 1905). Monsieur Krutwig écrit: "nous avons chauffé des solutions de sucre saccharose à 85° cent. *pendant 6 heures*, dans des vases en verre, en métal et, en présence de lamelles de zinc, de cuivre et de fer.

"*Aucune coloration ne s'est manifestée.* Il n'en est plus de même lorsqu'on ajoute au liquide quelques centièmes de bases alcalines ou alcalino-terreuses. Une coloration jaune apparait au bout d'un temps relativement court et le liquide devient de plus en plus foncé si on l'additionne préalablement de lévulose ou de dextrose."

Si l'on consulte les auteurs qui ont étudié spécialement le caramel et ses dérivés, (Péligot, Gillis, J. J. Pohl, Völckel, Maumené, Herzfeld, Stolle etc. . . . .) on voit qu'il faut enlever à la saccharose au moins deux molécules d'eau pour y parvenir il faut chauffer le sucre sec à une température d'au moins 190° cent. température jamais atteinte dans notre industrie (Völckel dit 210–220° et Stolle dit: "l'on voit donc par ce qui précède que la formation du caramel se produit par un chauffage à température constante 170 et 180° cent. *simplement* par perte d'eau). D'après M. Gilis qui dans son mémoire à l'académie des Sciences T. XIV page 590 (1857) décrit savamment les diverses réactions des trois substances carameline, caralène et carameline qui composent le caramel, le premier de ces corps se créerait à 190° centi. suivant la réaction:

$C^{12}H^{22}O^{11} = 2\ H^{2}O + C^{12}H^{18}O^{9}$
le deuxième $3\ C^{12}H^{22}O^{11} = 8\ H^{2}O + C^{36}H^{50}O^{25}$
le troisième $8\ C^{12}H^{22}O^{11} = 37\ H^{2}O + C^{96}H^{102}O^{51}$

On pourrait même ajoute-t-il "en graduant convenablement la température, obtenir ces trois produits d'une manière successive; ainsi le sucre exposé à 190° cent. jusqu'à ce qu'il ait perdu 10% d'eau se transformerait en caramelane à peu près pure. Après avoir subi l'action de la même température au point d'avoir perdu 14 ou 15% d'eau, il laisserait au contraire, un résidue riche en caramelène et enfin après une perte de 20% d'eau, il est totalement converti en carameline. Les produits qui résultent de l'action de la chaleur sur la glucose ressemblent beaucoup aux précédents mais ne sont pas identiques avec eux."

J'ai tenu à citer succintement les travaux trop oubliés d'un savant, afin d'étayer mon argumentation en faveur de la thèse que je défends depuis longtemps: *que la surchauffe temporaire et rapide des jus*, sirops et masses cuites n'est pas nécessairement et *inmanquablement destructive de saccharose;* j'ajouterai même que contrairement à ce qu'écrivait notre savant et consciencieux collègue M. Fr. Stolle dans son mémoire: "Sa nature chimique des produits de surchauffe des sucres" au 5ᵉ Congrès international de chimie appliquée, (Berlin 2-9 Juin 1903) *que le plus grand ami des solutions sucrées est sans contredit la chaleur judicieusement employée* qui éloigne d'elles tous les germes fermentescibles, tous les micro-organismes qui ne demandent qu'à s'en emparer; le tout est de savoir s'en servir même à 130° 140° cent. Monsieur Fr. Stolle écrit: "*le plus grand enemi du sucre est sans contredit la chaleur.* Nous savons que dans les phases de la fabrication ou le sucre est exposé pendant *longtemps à des temperatures élevées* il subit des transformations et changements plus ou moins visibles, reconnaissables à l'odeur, au goût et à l'oeil." Je ne puis admettre sa manière de voir.

De nos jours, avec les moyens économiques et pratiques de chauffage des jus en réchauffeurs à multiples circulations, en bannissant tout ce qui peut être chauffage par serpentins conséquememment par propagation moléculaire lente des calories dans des masses dormantes, en un mot, en faisant toujours circuler au maximum de vitesse possible, jus, sirop et masse cuite dans des faisceaux tubulaires divisant à l'infini les points de propagation des calories comme dans les appareils tubulaires Kestner à grimpage ou descendage; il n'y a plus à craindre comme au temps jadis, la décomposition du sucre par stagnation sur des serpentins surchauffés au moyen de vapeur à cinq voire même huit atmosphères, serpentins qui souvent sont partiellement découverts de sirop, ce qui permet la deshydratation de la saccharose et la formation du caramel ou de ses dérivés.

Certes en raffinerie et en sucrerie on a créé de plus ou moins fortes quantités de se corps complexe et excessivement colorant; certains usines mal outillées, mal dirigées, en créent et en créeront encore longtemps, mais j'insiste tout particulièrement sur ce que l'on peut ne pas développer de caramel et sur le travail qui se pratique à Marseille aux raffineries de Saint Louis, à Tirlement à la raffinerie Tirlemontoise, à Marcq en Baroeul à la raffinerie l'Abeille. Dans les deux premières usines, si l'on prend la moyenne du sirop de raffinade à cuire, sirop incolore et cristallin à 99.50 de pureté, ne réactionnant pas à la liqueur de Soldaïni et que l'on dilue la masse cuite obtenue par cuisson rapide de ce sirop, on voit que cette dilution de densité égale au sirop primitif, aura la même coloration et la même composition chimique. Il ne peut donc y avoir par la cuisson de produits purs, aucune décomposition du sucre, voire même en produits n'ayant comme ceux de la raffinerie de Marcq que 98.20 de pureté, sirop de raffinade renfermant de 0.100 à 0.160 de glucose %. La composition de la mélasse de cette usine, qui travaille par un procédé de raffinage qui m'est personnel, ne nécessitant pas un atome de noir en grain ni de noir en poudre est la suivante:

Extrait sec correspondant 78 Densité picnométrique 1399	sucre par polarisation	46.40
	glucose, liqu. Felhing	0.94
	centres, inc. sulfu.	10.76
	Matière organiques par différence	19.90
Quotient de pureté des divers sucres		60.69
Quotient de pureté du sucre par polarisation		59.48
Coefficient salin		4.31
Coefficient organique		2.33
Cendres % de sucre (polarisation)		23.19
Matières organiques % de sucre		42.88
Glucose % de sucre		2.03

Réaction alcaline au papier de tournesol sensible et neutre au phénolphtaléine.

Cette mélasse de composition normale dans ses proportions entre les divers corps qui la composent, correspond máthématiquement aux divers sucres bruts mis en oeuvre.

A la raffinerie de l'Abeille on travaille de 12 à 15% de sucre cristallisé par rapport aux divers sucres roux, à environ 90° de titrage qu'on y traite par lessivage Langen. Si l'on prend en charge tous les éléments autres que le sucre qui entre en fabrication, sels, glucose, matière organiques, à peu de chose près, on retrouve mensuellement dans un produit final dénommé mélasse, tous ces éléments dans les mêmes proportions où ils étaient renfermés dans les sucres; je me demande alors où se trouvent, en raffinerie bien et judicieusement conduite, les décompositions de sucre par surchauffage, cuisson et recuisson des produits, fermentation, double décomposition, comme tend à le faire croire le mémoire de Monsieur le professeur docteur E. von Lippman (Halle S. Saale au Ve Congrès de chimie appliquée de Berlin). Dans ce mémoire intitulé, "les pertes de sucre en raffinage, ce savant écrit:" "quelle explication peut-on donner en l'occurence, de la disparition apparenta de ces 0.300 pour cent de sucre? à mon avis, une *seule* est possible, savoir: les destructions pendant la cuite ne se bornent pas à transformer le sucre en matières non sucre, stables, qui restent dans les sirops et masse cuite, mais le non sucre qui se trouve dans les solutions est décomposé *à son tour*, en formant des quantités sensibles de combinaisons volatiles et gazeuses qui s'échappent dans les vapeurs ammoniacales et les eaux de condensation."

C'est pourquoi les raffineurs aussi avancés que les Desbief, Beauduin, Raeymaeckers, Bergé etc. . . . ont compris qu'en tête du travail de raffinerie il fallait un produit aussi pur, aussi cristalin que possible, ne pouvant donner de réactions secondaires, la saccharose pure se protégeant elle-même contre toute atteinte de la surchauffe, aussi longtemps qu'il n'y a pas de deshydratation de sucre; il ne saurait y en avoir, attendu qu'il y a de l'eau d'interposition et non de combinaison à évaporer; c'est pourquoi les expériences du professeur A. Herzfeld relatées par le professeur von Lippman, se rapprocheront plus de ce qui se passe industriellement dans les raffineries utilisant tous faisceaux tubulaires pour chauffage, concentration, cuisson et recuisson de produits, que ce qui s'y passait il y a dix ou vingt ans, ou ce qui se passe encore dans les raffineries qui n'ont pas évolué. Monsieur von Lippman en se basant sur les recherches nombreuses qu'il fit, disait: "je suis arrivé à la conclusion que les décompositions en question ont lieu à la cuite. Ces conclusions ont été, tant que je sache, reconnues depuis généralement comme exactes. Si parfois en a essayé d'en douter, en se basant sur les essais de Herzfeld, c'est à tort, d'abord parce que les essais d'Herzfeld n'avaient nullement pour but de poursuivre les modifications de claircés à si haute concentration et puis, parce que ces essais ont été faits au moyen d'autoclaves chauffés dans un bain d'huile; et comme Herzfeld l'a dit plus tard, dans ce cas les décompositions peuvent être jusqu'a dix fois moindres qu'en cuisant avec de la vapeur à 130° par exemple."

J'ai tenu à citer ces quelques phrases, car il est certain que les essais du docteur Herzfeld avaient fortifié ma conviction que la destruction du sucre à la cuite était fonction de bien des conditions mauvaises qu'on pouvait pratiquement éviter, ce que je me suis toujours efforcé de faire et, je dois le dire, avec un plein succès; car je ne crains pas en cuisson rapide, dans un appareil Kestner continu, d'employer de la vapeur à 5 atmosphères, conséquemment à 158° cent; il est vrai que la clairce à cuire ne fait que passer, étant au point de cuite en quelques secondes, ce qui demande de 40 à 60 minutes dans une cuite tubulaire ordinaire et deux, trois, quatre heures pour parvenir au même résultat avec de la vapeur de décharge à 5 dixièmes d'atmosphère. Toute cuite de raffiné doit être aussi rapide que possible et alors, quelle que soit la vapeur employée, dans le faisceau tubulaire, de 0.5 à 5 atmosphères, le produit pur, cuit sous un vide de 60 à 62 centimètres, réchauffé avant coulage à 90 à 95°, ne saurait renfermer de caramel ou l'un de ses dérivés, pas plus que ce même produit cuit en marche continue sous pression de 2 atmosphères, soit 133° cent. Toutefois, dans certaines circonstances, la masse cuite pourra renfermer des produits de la nature de la dextrine; je serais assez enclin à me rallier, industriellement s'entend aux conclusions très acceptables de M. le docteur Stolle qui écrit: "j'espère toutefois avoir démontré que la caramelisation en travail normal n'est pas aussi forte qu'on le supposait jusqu'ici; de plus, l'action d'une température élevée a pour effet d'augmenter plutôt la teneur en produits de la nature de la dextrine. Les pertes dues aux composés du caramel sont très petites quand une bonne circulation de la masse cuite dans l'appareil à cuire ne permet pas à la masse de sucre d'être longtemps en contact avec les serpentins de vapeur."

Vous remarquerez que M. Stolle parait encore en 1903 de serpentins de vapeur et que, dans mon étude, et depuis longtemps, je conseille mon 'seulement la cuite tubulaire sous vide ou sous pression, mais encore tous les chauffages et concentrations en faisceau tubulaire Kestner ou autre, jus et sirop étant à l'abri de l'air; alors, mais seulement alors, le caramel aura radicalement disparu de l'industrie sucrière autant en raffinerie qu'en sucrerie de betterave ou de canne. Dans une communication ultérieure, j'indiquerai les moyens d'éviter en sucrerie que les matières salines organiques autres que le sucre, ne viennent colorer les produits.

A la sucrerie centrale d'Escaudoeuvres (France) où on utilise le procédé si rationnel et si simple de sulficarbonatation de J. Weisberg, les masses cuites diluées à la densité du jus avant évaporation, sont plus décolorées que ces jus et les cristallisés de sucrerie sont superbes.

QUELQUES PARTICULARITÉS NOUVELLES SUR L'EMPLOI DE L'ANHYDRIDE SULFUREUX ET DES HYDROSULFITES DANS L'INDUSTRIE SUCRIÈRE

A. Aulard
Bruxelles, Belgium

Avant d'aborder le sujet de ma communication, permettez-moi un retour sur le passé.

En relisant ce qu'écrivaient nos devanciers, ce que je fais souvent et toujours avec fruit, il m'a fallu bien des fois reconnaître que nos "soi-disant" découvertes chimiques et bien des perfectionnements techniques ne provenaient que de l'ignorance dans laquelle nous étions de ce qu'avaient écrit et même fait breveter nos aînés.

(La somme des brevets *vieux neufs* devient vraiment par trop considérable.)

Si on relit les travaux de Proust, qui datent de plus de cent ans! dans le Journal de Physique de Paris de 1810, ceux de Drapiez, en 1811, Perpère 1812 et surtout si on lit attentivement les brevets de Dubrunfaut en 1829, celui de Stollé en 1839 et celui si clair, si net de Melsens, professeur de chimie à Bruxelles, du 26 Juillet 1849 (n° 8560), on ne peut s'empêcher de se dire que rien de nouveau n'a été fait en sucrerie-raffinerie au sujet de l'emploi de SO_2 gazeux, ni des bisulfites, hydrosulfites, aux noms étranges d'aujourd'hui, Blankite, Redo, etc. . . Un fait nouveau seul se dégage du mode d'emploi de SO_2 provenant de la combustion du soufre ou de l'anhydrid sulfureux liquéfié et ce procédé sur lequel j'ai fait au VII° Congrès international de chimie appliquée de Londres, une communication très documentée, nous fut enseigné par notre savant collègue J. Weisberg, dans son "Etude pratique sur l'emploi de l'acide sulfureux dans l'industrie sucrière" (Bulletin de l'Ass. des Chimistes de Sucrerie et Distillerie de France et des Colonies—années 1903–1904).

En commentant et en justifiant son brevet de 1849, feu le professeur Melsens, duquel en ce Congrès de chimie appliquée j'aime à rappeler les éminents travaux, d'autant plus que nous sommes compatriotes, s'exprimait ainsi qu'il suit:

"A la propriété antiseptique, à la faculté d'absorber le gaz oxygène de l'air, les bisulfites de chaux, de baryte, de strontiane, de soude, etc. joignent encore les caractères d'énergiques déféquants.

"Le bisulfite de chaux décolore instantanément et assez complètement les matières colorées qui existent toutes formées dans la canne et la betterave; il prévient la formation des matières colorées que l'air produit par son contact avec les pulpes; *il empêche également la production de celles qui naissent pendant l'évaporation* et surtout de celles qui exigent pour se former le concours de l'air et d'un alcali libre.

"Ainsi les bisulfites peuvent être utilisés dans les opérations qui ont pour objet l'extraction du sucre de la canne, de la betterave, *du maïs*, etc. Le bisulfite de chaux, par exemple agit:

"1°.–comme corps antiseptique par excellence, prévenant la production et l'action de tout ferment;

"2°.—comme corps avide d'oxygène, capable d'empêcher les altérations que sa présence fait naître dans les jus.

"3°.—comme corps déféquant, qui, à 100°, clarifie les jus et les débarrasse de toutes les matières albumineuses ou coagulables.

"4°.—comme corps décolorant pour les couleurs préexistantes.

"5°.—*comme corps anti-colorant capable au plus haut degré de s'opposer à la formation des matières colorées.*

"6°.—comme corps capable de neutraliser tous les acides nuisibles qui pourraient exister ou naître dans les jus, en leur substituant un acide presque inerte: *l'acide sulfureux.*"

Depuis Melsens, et il y a 73 ans de cela! nous ergotons, nous présentons sous de nouvelles faces et phrases ce qu'il a si bien défini; mais nous n'avons rien fait de mieux que ce qu'il indiquait; lamentablement, nous avons marqué le pas ou plutôt rétrogradé dans l'emploi judicieux de SO_2. On s'étonne que malgré les volumes publiés sur l'emploi de l'anhydride sulfureux dans l'industrie sucrière (j'en ai publié deux, 1897 et 1899, au sujet d'un concours organisé par le Syndicat des fabricants de sucre de

France[1], il y ait encore des sucreries qui ne l'emploient pas ou qui l'utilisent si mal qu'elles feraient mieux de ne pas s'en servir.

Lorsque l'on suit bien toutes les prescriptions de la sulfi-carbonatation de J. Weisberg, comme le font les sucreries de Saint Trond (Belgique), d'Escaudoeuvre, de Beauchamp, de Masny (France), etc. on obtient des résultats de décoloration et de fluidité des produits tels, que l'emploi des adjuvants, blankite, Redo, bisulfite, hydrosulfite, etc. *sont absolument inutiles:* je l'ai dit maintes fois déjà, mais ne saurais trop le redire; si l'on veut que dans l'emploi de SO_2 liquéfié, tout l'anhydride sulfureux gazeux à 99% de pureté soit utilisé, il faut comme à Escaudoevure, à Saint Trond, etc., employer un sulfiteur continu, très simple, permettant l'untilisation complète de SO_2. M'appliquant tout spécialement à la propagation d'un travail normal économique et rationnel en sucrerie et raffinerie, j'ai été conduit pour utiliser SO_2 au maximum, de chercher un appareil continu fort simple, réalisant tous les desiderata; après divers tâtonnements, j'y suis hereusement parvenu et aujourd'hui une sucrerie qui travaille 500 tonnes de betteraves par 24 heures et qui utilise SO_2 liquéfié, n'a besoin que d'un sulfiteur continu de mon invention, coûtant approximativement mille francs. Si la même usine employait SO_2 provenant de la combustion du soufre, deux appareils reposant sur le même principe, mais d'un diamètre plus grand, seraient nécessaires. Lorsqu'on a pratiqué comme moi la sulficarbonatation J. Weisberg dans diverses usines et, l'an dernier, avec des betteraves aussi anormales que celles dues à la sécheresse, on reste stupéfait du peu d'empressement que mettent les industriels à utiliser un procédé pouvant s'appliquer en toutes circonstances et avec grand profit sur les jus limpides de première carbonatation. Ce mode d'emploi permet de laisser en deuxième carbonatation une alcalinité fixe, stable et d'avoir toujours à l'évaporation des produits franchement alcalins, alcalinité qui, quelle que soit la betterave mise en oeuvre, ne rétrograde pas. C'est aussi le mode de sulfitation qui élimine le maximum d'organates calciques; c'est ainsi que l'an dernier, dans une grande sucrerie française, le jus filtré de deuxième carbonatation ne renfermait en moyenne pour toute la campagne que 0,0041 de CaO par 100 cc et le sirop à 30–32° Baumé, 0,017 de CaO%. Au sujet de ce travail, M. l'Ingénieur Paul Marcus, s'emprimait ainsi qu'il suit dans le "Journal des fabricants de sucre de France":

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[1] **42, Rue du Louvre, Paris.**

"*Sulficarbonatation.*—L'effet obtenu se manifeste par une très forte décoloration qui atteint en moyenne 50% et reste *acquise au cours du travail ultérieur.* Les sirops provenant des jus traités par le procédé Weisberg, sont peu teintés et d'une faible viscosité; ceux que nous avons vus dans les derniers jours de cette campagne étaient de la plus grande limpidité; ils n'étaient, malgré leur très haute concentration, guère plus colorés que beaucoup de jus filtrés de deuxième carbonatation résultant du traitement habituel.

"De l'aveu même des dirigeants de la sucrerie d'Ercau d'oeuvre, l'application bien comprise et bien dirigée de la sulficarbonatation J. Weisberg a contribué pour la plus large part à l'obtention de beaux cristallisés blancs extra, de la première à la dernière cuite, dans cette campagne si difficile et désormais fâcheusement historique de 1911–12."

Cette narration désintéressée et contrôlable, d'un procédé qui a rendu pratique l'emploi raisonné de SO_2 décidera probablement mes confrères de ce côté de l'Atlantique à le conseiller aux usines qu'ils dirigent chimiquement. Ici plus que partout ailleurs, je crois que le procédé donnerait ses pleins effets, tout terrain nouveau consacré à la culture de la betterave sucrière donnant toujours, durant les premières années, des betteraves organiques qui entraînent en fabrication la formation d'organates calciques; j'ai observé la chose en Espagne, en Italie, en Russie, voire même dans les polders hollandais; c'est pourquoi je ne saurais trop vous engager à employer aussi judicieusement que dans quelques usines belges, françaises et russes, le procédé de sulficarbonatation Weisberg; il laissera certainement dans vos arrières produits et mélasses *moins de sulfates et de sulfites* que le même produit provenant des mauvaises sulfitations ordinaires, car SO_2 est *scientifiquement et judicieusement employé* et il est lui-même son producteur d'hydrosulfites de potasse et de soude dont nous connaissons tous les bienfaisants effets.

SUR LA CRISTALLISATION DE LA SACCHAROSE EN MILIEU PLUS AU MOINS IMPUR

A. Aulard
Bruxelles, Belgium

Dans une étude déjà ancienne (Bull. Ass. Belge des chimistes 1891) sur la raffinose et la cristallisation du sucre de séparation, je m'exprimais ainsi qu'il suit sur la cristallisation de la saccharose en milieu plus ou moins impur:

"Tous les chimistes savent que la saccharose $C^{12}H^{22}O^{11}$ ou sucre cristallisable, cristallisé en prismes, clinorhombiques ou binaires hémiédriques, durs et anhydres."

La saccharose ne saurait cristalliser que chimiquement pure, mais plusiers petits cristaux soudés entre eux peuvent interposer entre leurs arêtes enchevêtrées quelques parcelles d'eaux mères; de là vient que le sucre semble grisâtre ou jaunâtre suivant le milieu dans lequel les cristaux ont été nourris. Il importe beaucoup dans les sucreries, qui veulent produire du sucre de consommation directe, cristallisés de choix, que la masse cuite soit aussi décolorée et aussi fluide que possible. Cette décoloration et cette fluidité atteindront le maximum par l'emploi judicieux de la sulficarbonatation J. Weisberg; mais il ne suffit pas que la masse ait les qualités requises énumérées ci-dessus; il faut encore qu'à un moment de la cuite, on ne vienne pas, par une alimentation irraisonnée et intempestive de sirop moins riche et plus dense, compromettre la régularité des cristaux; elle ne l'est déjà que trop. En admettant une alimentation régulière en sirop de pureté, par exemple de 92° et en analysant, en observant ce que se passe dans un appareil à cuire, en prélevant souvent des échantillons qu'on examinera à la loupe ou au microscope, on observera que peu après la cristallisation, tous les petits cristaux sont bien conformés, à cristallisation clinorhombique parfaite; petit à petit, en grossissant au fur et à mesure de leur alimentation et de ce que la masse cuite s'élèvera dans l'appareil, ils se déformeront sous l'influence de l'eau mère saline et organique qui les baigne et qui passera d'une pureté de 92° à 84° voire même 80°. Il se forme dans l'appareil des couches de composition saline et organique différentes; l'introduction du sirop nouveau se faisant toujours par le bas, la base rhombe des cristaux qui gravitent dans le sens de l'appel de vide s'élargit; la partie la plus lourde étant tournée vers le bas, trouve un milieu plus favorable à sa nutrition en dessous qu'en dessus, suivant en cela des principes déterminés dans la cristallographie des corps; par contre, sous la résistance qu'offre aux cristaux au milieu défavorable à leur développement normal, milieu plus pauvre se trouvant vers le haut de l'appareil, là ou les sels de potasse et de soude et les matières organiques vont s'accumulant, les cristaux s'aplatissent et s'affinent en un endroit quelconque d'une le leurs arêtes ou d'un de leurs angles; ils accusent alors des cristaux de toutes les formes possibles, voire même en aiguille, comme dans les sucres provenant de l'extraction du sucre des mélasses, (séparation et barytage etc. . . .), le mal va s'aggravant encore si dans l'appareil à cuire, on rentre en cuisson à la fin de la cuite, des sirops denses d'une pureté inférieure à celle de l'eau mère baignant les cristaux; bien souvent alors les cristaux se rongent et se fractionnent, même, au lieu de grossir normalement sur toutes les faces. Il faut donc, lorsqu'on veut obtenir de beaux cristallisés en premier jet, que la cuite tubulaire, préférablement à toutes les autres, n'ait qu'une durée des plus limitées, 6 à 8 heures au maximum; il faut que le sirop d'alimentation soit toujours dense, (de 56 à 58 Brix à 19°c) d'une température de 80 à 85°c. et aussi fluide, aussi pur, aussi décoloré que possible à son entrée dans l'appareil à cuire; alors en menant la cuite rapidement, sans mélange, sans rentrée d'aucun égoût de turbinage, on obtiendra des cristaux très réguliers, se rapprochant de leur cristallisation classique.

Si, au contraire, la cuite est lente avec des rentrées plus ou moins copieuses d'égouts pauvres, les cristaux se déformeront et l'aspect du sucre après turbinage sera terne, parce que beaucoup de cristaux auront perdu leur forme naturelle. La cuite sera coulée à 8% d'eau à 84°–85° C dans des cristalisoirs Ragot, très supérieurs aux autres parce que les points de refroidissement sont en mouvement dans une masse chaude et fluide. Le turbinage s'effectuera 6 heures au maximum après la coulée de la cuite, la température de la masse étant encore de 60° cent. Il faudra donc conduire la réfrigération de façon à avoir une chute de température de 4° à l'heure. Durant le malaxage et le refroidissement de la masse cuite, on ajoutera des égouts de turbinage saturés et chauds de 75° à 80° cent. de telle façon qu'au turbinage la masse aura de $8\frac{1}{2}$ à 9% d'eau; elle sera fluide et tiède à 60° cent. comme dit ci-dessus; on obtiendra alors de superbes cristallisés très brillants et non ternes, qui toutefois, ne subiront qu'une comparaison relative avec les cristallisés de raffinerie fabriqués avec des produits à 98°–99° de pureté et forcément de cristallisation plus classique et plus uniforme.

C'est ainsi que cette cristallisation apparait admirablement régulière dans les cuites de raffiné à 99, 50° de pureté de la raffinerie Tirlemontoise à Tirlemont, (Belgique) parce que la cuite est rapide, coulée en moules Adant et que les cristaux petits, mais uniformes et brillants, ne subissent aucune déformation par suite de l'impureté du sirop-mère dans lequel ils sont rapidement nourris. Lorsqu'on prend un morceau de sucre et qu'on l'humecte d'une eau artificiellement colorée, il s'imprègne et se teint régulièrement, ce qui n'a pas lieu avec des raffinés préparés dans des milieux plus impurs; il faut donc en tête du travail, autant en raffinerie qu'en sucrerie, avoir les produits les plus purs et les plus fluides possible, cuire rapidement, de façon à conserver aux cristaux leur forme clinorhombique et toute la limpidité brillante qui les fait se rapprocher de celle de petits diamants dont ils ont la composition (carbone pur). C'est pourquoi les procédés de cuisson continue, P. Kestner, ou de cristallisation par refroidissement d'une masse chaude saturée en sucre Druelle-Say, Lambert, Mastaing et Delfosse Lagrange, n'ont à mon avis pas encore dit leur dernier mot.

Dans le procédé Kestner judicieusement appliqué et compris, il y a une idée nouvelle qui nous affranchirait des appareils encombrants que nous utilisons aujourd'hui, idée qui, fera son chemin parce qu'elle est basés sur des lois de physique et de cristallographie applicables industriellement. Les cristaux aussi petits soient-ils qui se forment dans une masse pure ou impure, sont toujours de même forme si on les élimine vite de la masse dans laquelle ils ont pris naissance; ils la conservant d'autant mieux qu'ils auront moins subi l'influence déprimante du milieu de l'eau mère dans laquelle ils sont maintenus en mouvement se rodant les uns sur les autres. Je ne doute pas que Monsieur P. Kestner qui a déjà doté l'industrie sucrière d'appareils concentrateurs des jus très intéressants, appareils rompant avec une construction emcombrante et surannée, ne parvienne également à réaliser la suite continue simple et pratique si, bien entendu, Messieurs les industriels veulent rompre avec des types de sucre également surannés.

(*Résumé*)

ETUDE CHIMIQUE SUR LA CARBONATATION

K. Andrlík et V. Staněk

Vu les différentes modifications employées pour la carbonatation dans la pratique industrielle nous n'avons pas cru sans importance d'étudier de plus près au point de vue chimique l'effet complexe que produit la carbonatation sur les jus bruts.

Nous nous sommes efforcés particulierement de trouver une methode précise, qui nous permettrait de reconnaitre les avantages qu'offrent les divers procédés industriels. Voici les trois points, qui ont été l'objet des nos recherches.

1) Quelle est la différence de polarisation qu'on peut trouver dans les jus de diffusion apres une triple carbonatation, éventuellement après le chauffage avec la chaux.

2) Quels sont les effets d'une triple carbonatation sur la pureté et sur la composition des jus, traités avec des quantitées de chaux différentes.

3) Quel est l'effet de la triple carbonatation, calculé de la composition et de la quantité des écumes de carbonatation en employant des quantitées de chaux différentes. Dans le cours de nos recherches nous avons observé ce qui suit:

1) Pendant la triple carbonatation des jus la polarisation initiale diminue; cette diminution varie de 0.04 jusqu'à 0.16% calculé sur le poids du jus brut et elle semble être proportionelle à la quantité de chaux employée. Le chauffage des jus bruts au bain marie à 100° C pendant 10 minutes avec 1% de chaux diminue également la polarisation du jus brut de 0.1 jusqu'à 0.12% sur le poids du jus.

2) L'augmentation de la chaux de 1.5 à 3.5% sur le poids du jus ne se fait sentir que dans le cas de quelques jus bruts, notamment de celles qui accusent une pureté inférieure à 88%.

Dans ce cas la l'effet de la carbonatation se montre par une élévation de la pureté du jus et une petite diminution des cendre et de l'azote.

3) L'augmentation de la chaux—par exemple de 1.5 à 3.5% sur le poids du jus bruts—à la carbonatation produit un effet incontestable à la couleur du jus; on la trouve plus faible dans le cas où la quantité de chaux était plus élevée.

4) On éloigne en moyenne 0.25% de matières organiques en plus, calcule sur le poids du jus brut, si l'on emploi des quantités de chaux à la carbonatation plus élevées par exemple de 1.5 jusqu'à 3.5%, supposé que l'on ait apprécié l'effet aumoyen de l'analyse chimique usuelle, c'est-à-dire par dessication à poids constant à 105° C.

5) L'analyse élémentaire des écumes de carbonatation a montré que l'analyse usuelle fait parraître l'accroît d'épuration quant aux matières organiques produit par l'augumentation de la chaux deux jusqu'à trois fois plus grand.

La présence de l'eau de combinaison dans les écumes était demontré en appliquant à la fois les dites methodes analytiques aux écumes obtennues par la carbonatation de la chaux

1) suspendue dans l'eau,
2) suspendue dans une solution de saccharose,
3) aux écumes de la carbonatation des jus bruts.

(*Résumé*)

SUR LES RELATIONS ENTRE LA RICHESSE SACCHARINE DES RACINES ET LES CARACTÈRES CHIMIQUES DES DESCENDANTS D'UNE BETTERAVE-MÈRE DANS LE PREMIÈRE GÉNÉRATION

K. Andrlík et J. Urban

La richesse saccharine des racines provenant d'une mère en première génération peut correspondre a un poids très différent des racines, poids qui peut varier dans les limites de la variabilité du caractère en question.

Pour les moyennes des richesses saccharines et les moyennes de poids des racines des mêmes individus la loi de la correlation n'est pas valable du tout ou elle ne se fait sentir que d'une façon presqu'insignifiante. Elle apparait plutôt chez les moyennes des poids du feuillage où correspondent aux moyennes supérieures de richesse saccharine des poids moyens inférieurs de feuillage et vice-versâ.

En ce qui concerne la relation entre la richesse saccharine et la matière sèche des racines et des feuilles nous avons trouvé qu'une même richesse saccharine peut correspondre à des matières sèches différents des racines et de feuillage et peut varier dans les limites de la variabilité des matières sèches des racines et du feuillage.

Les moyennes des richesses saccharines inferieures correspondent à des moyennes inférieures de matières séches et inversement; cela à lieu pour les racines comme pour le feuillage.

Il y a donc proportion directe entre les caractères en question.

Quant à la relation entre la richesse saccharine des racines et leurs cendres et les cendres des feuilles nous avons observé qu'à une même richesse saccharine peuvent correspondre des cendres

et que ces différences se trouvent dans les limites de la variabilité des cendres des racines et du feuillage de la même ligne.

Les moyennes de richesse saccharine supérieures correspondent à des moyennes de cendres qui ne sont que faiblement supérieures pour les racines mais sensiblement supérieures pour les feuilles et vice-versâ.

Il y a donc ici proportion directe dans les deux cas, mais plus accentuée dans le second.

L'étude de la relation entre la richesse saccharine des racines et la teneur en azote des racines et du feuillage nous a montré en premier lieu qu'à une richesse saccharine donné peuvent correspondre des teneurs en azote extrêmment variables pour les racines et pour les feuilles. Le différences ont pour limite l'amplitude de la variabilité de ce caractére c. à d. de la teneur en azote des racines et du feuillage.

Les moyennes des richesses saccharines supérieures correspondent à des moyennes de la teneur en azote des racines et du feuillage égales ou un petit peu plus élevées et vice-versâ.

(*Résumé*)

VARIABILITÉ DE LA CONSOMMATION DE L'AZOTE DES DESCENDANTS D'UNE BETTERAVE PORTE-GRAINE DANS LA PREMIÈRE GÉNÉRATION

K. Andrlik et J. Urban

Le consommation de l'azote chez les descendants d'une betterave porte-graine n'est pas egalle même dans le cas où la culture de la betterave a ed lieu dans des conditions pratiquement identiques; elle ne l'était pas non plus pour les descendants ayant une richesse saccharine égale.

Elle est probablement regie par le loi de la variabilité fluctuante, trouvé par Quetelet-Galton.

Cette variabilité se laisse exprimer par une courbe ressemblante à la courbe binomialle.

L'amplitude de la variabilité de la consommation d'azote chez les individus de la même linie s'évaluait à 202.6% de la consommation moyenne de la même linie, c'est-à-dire à 1.98 g pour une plante.

La quantité de sucre trouvé dans les racines de la ligne étudiée présentait également une fluctuation, probablement soumisse à la loi de le variabilité fluctuante.

La proportion de l'azote consommé sur 100 partie de sucre differait également d'un individu à l'autre.

L'amplitude de cette variabilité était evaluée à 81.8% de la consommation moyenne d'azote, qui pour cette génération était de 3.67 parties sur 100 parties de sucre et une plante.

Les individus plus riches en sucre consommait en moyenne moins d'azote et vice-versâ l'amplitude de la variabilité de cette consommation était donc inférieure.

Par la sélection basée sur la polarisation les descendants à consommation d'azote plus élevée sont probablement éliminés.

(*Résumé*)

VARIABILITÉ DE LA COMPOSITION CHIMIQUE DES DESCENDANTS D'UNE BETTERAVE PORTE-GRAINE DANS LA PREMIERE GÉNÉRATION

K. Andrlik et J. Urban

En analysant les racines et les feuilles des descendants d'une betterave porte-graine dans la premiere génération on pouvait constater une différence remarquable dans leurs composition chimique.

De même que les caractères extérieurs varie aussi la composition chimique des descendants d'une betterave mère et cela dans les limites données par la variabilité fluctuante.

Ce phénomène nous l'avons constaté en dosant la matière sèche les cendres et l'azote dans les racines et les feuilles de 100 individus.

Chacun de ces caractères chimiques indique une variabilité, qui se laisse exprimer par une courbe qui ressemble à la courbe binomiale de Quetelet-Galton.

Nous avons déterminé l'amplitude de la courbe de variabilité et l'avons exprimé ensuite par la valeur moyenne des caractères volables pour les descendants de la même betterave mère.

Pour plus de clarté nous avons representé ses variations grafiquement par des courbes.

Nous avons nottamment constaté:

Que l'amplitude de la variabilité de l'azote dans les racines s'évalui à 88.2% de la valeur moyenne de ce caractère chez les descendants étudié (0.248%);

Que l'amplitude de la variabilité de l'azote dans les feuilles s'évalue à 67.1% calculé sur la teneur moyenne en azote des mêmes descendants (0.325%);

Que l'amplitude de la variabilité des matières sèches dans les

racines s'évalue à 33.4% calculé sur la valeur moyenne de ce caractère (23.56%);

Que l'amplitude de la variabilité des matières sèches dans les feuilles s'évalue à 71.9% sur les matières sèches moyennes des descendants étudiés (13.78%);

Que l'amplitude des cendres dans les racines s'évalue à 64.7% de cendre moyenne des racines appartenant à la même génération (0.692%);

Que l'amplitude de la variabilité des cendres dans les feuilles est de 81.8% de cendres moyennes dans les feuilles des mêmes descendants (3.25%).

En outre nous avons démontré la variabilité fluctuante du poids des feuilles dans la période de végétation ou ce poids atteint son maximum. L'amplitude de cette variabilité etait évalué à 189% du poids moyen des feuilles des descendants étudiés (357 g).

L'amplitude de la variabilité du poids des racines était évaluée a 193% du poids moyen des racines de la même génération (331 g).

Nous avons déterminé de nouveau l'amplitude de la variabilité de la richesse en sucre pour les descendants d'une mère. Elle se monte à 28.5% de la richesse moyenne des descendants considérés (16.3%).

Toutes cettes variabilités sont valables pour la période de végétation ou le develloppement des feuilles avait atteint son maximum.

A REVISION OF THE HUNDRED POINT OF THE SACCHARIMETER

FREDERICK J. BATES AND RICHARD F. JACKSON
Washington, D. C.

For the purpose of checking the accuracy of saccharimetric analysis, the polarization of highly purified sugar solutions was measured. For the preparation of pure sucrose the method of crystallization from aqueous solutions after concentration in a vacuum boiling apparatus was developed. The sugar thus prepared did not differ essentially from that precipitated by alcohol. A study of the purified sugar showed the absence of ash and a negligible quantity of reducing substances. The experiments on reducing sugars showed the effect of sucrose on alkaline copper solutions and in the calculations this effect was taken into consideration. The velocities of caramelization of sugar at various temperatures was measured and a curve plotted indicating the length of time needed at each temperature to produce a quantity of caramel equivalent in reducing power to .01% invert sugar. The data are: 79.5°, 1.8 hrs.; 66.6°, 10.9 hrs.; 50.0°, 107 hrs.; 39.0° 478 hrs. The results prove that caramelization occurs at comparatively low temperatures, the effect taking place spontaneously, if slowly, at laboratory temperatures. The allowable time of heating as determined by the caramelization curve was applied to moisture elimination. A combination of high temperature and high vacuum was relied upon to dry the sample. Solutions for polarization were prepared, both gravimetrically, by reference to density tables, and volumetrically. The Specific Rotation of the normal solution was measured on a precision polarimeter for wave length 546.1 and found to be 78.385° at 20.00°C. By the use of a quartz plate, which had been certified by the Physikalisch-Technische Reicheanstalt and the Bureau of Standards, the scale correction of a saccharimeter was found and the correction applied to the polarization of the normal sugar solutions. These latter read not 100.00° but 99.91. The Herzfeld-Schonrock standard was concluded to be in error. If so, the new Conversion Factor for $\lambda = 589.25$ was computed to be 34.626 and that for $\lambda = 546.1$ was 40.707.

A CONSTANT TEMPERATURE LABORATORY FOR THE POLARIZATION OF SUGARS

C. A. Browne
New York, N. Y.

Since the installation in May 1909 at the New York Sugar Trade Laboratory of a cooling equipment for maintaining a temperature of 20°C during the warm season of the year, a large number of inquiries have been received by the writer regarding plans of construction, cost of equipment, expense of operation, method of temperature control and many other questions pertaining to the general subject of refrigeration for the laboratory. In the present paper the writer wishes to answer a few of such inquiries, and while well aware that the conclusions obtained from one set of conditions cannot be applied to all laboratories he nevertheless hopes that the results of his experience may be of some benefit to those seeking information along this line.

In the climate of New York a laboratory can be maintained without difficulty at 20°C for about 200 working days in the cooler months of the year by careful regulation of the heat supply and ventilation. In the warmer months of the year, or for about 105 working days, when the outside temperature exceeds 20°C artificial refrigeration must be resorted to in order to maintain standard conditions.

As to the requirements of a refrigerating equipment necessary for the purposes of a sugar laboratory, we may name the following: (1) rapid cooling of the laboratory (from temperatures of 30°C or more) to 20°C and maintenance of this temperature for as long a time as may be desired, the deviation from 20°C not to exceed 1°; (2) constant renewal of the air supply necessary for perfect ventilation; (3) complete absence of condensation of moisture upon the walls of the laboratory or upon apparatus; (4) absence of vibration from the refrigerating machinery which might affect the adjustment of polariscopes or other instruments.

There are of course other essentials, such as constancy of power and water supply, economy of operation, ease of control, etc., but these are of too obvious a character to require discussion.

The constant temperature room of the New York Sugar Trade Laboratory is approximately 24 feet long, 18 feet wide, and 10½ feet high. This space is largely taken up by working tables for the making up of solutions and filtering and by a polariscope cabinet containing 3 saccharimeters. The entire equipment is sufficient for the accommodation of 5 chemists and for the polarization in duplicate of a maximum of 150 samples of sugar per day. °The daily average of samples tested is, however, much less than this being about 60 per day. About 75% of these samples come from the port of New York, the remainder arriving from Philadelphia, New Orleans, Galveston, Boston, and the Canadian ports Halifax and Montreal. The samples thus received represent practically all of the raw cane sugar imported into the United States and Canada by way of the Atlantic Seaboard.°

The equipment of the constant temperature laboratory, as regards insulation, refrigeration, and ventilation, is briefly as follows:

Insulation. All the walls of the laboratory were not insulated but only those surfaces whose structure or position afforded excessive radiation towards outward heat. The surfaces thus insulated were the ceiling (separated by an air space from the tar and gravel roof of the building,), the wall and vestibule surrounding the entrance, and the sectional partition dividing the laboratory proper from the machinery space. The side walls of 2 in. plaster and the front walls of 12 in. brick covered with plaster were not insulated. All windows, however, were made double.

The insulating material employed upon the ceiling and wooden partitions consisted of ½ in. hair felt between heavy paper overlaid with matched boards of ⅞ in. tongue and grooved vine. The entrance to the laboratory consisted of a heavy insulated door of the ordinary cold storage type.

Refrigeration. The refrigerating machinery consisted of an 8 H.P. ammonia compressor rated at 5 ton refrigerating capacity per 24 hours. °The compressor was single acting, enclosed (with shaft and crank bearings running in oil), and with two cylinders (5 in. diameter and 9 in. stroke).° The compressor was driven by a 7.5 H.P. field control electric motor, the transmission being affected by a belt whose tension was regulated by an idler pulley. The speed of the motor could be varied between 375 and 580 revolutions per minute and that of the compressor fly wheel (1000 lbs) between 52 and 72 revolutions per minute. °The maximum work of compression coming at two points in each revolution caused an irregular tightening and slackening of the belt, but this was largely taken up by the spring of the idler, so that no difficulty was experienced in the work of transmission.° The compressor, which weighed in all 3600 lbs. was mounted upon a heavy platform to the outer wall of the building. No inconvenience from vibration was experienced at any speed or load of the machine.

During the operation of the compressor the hot ammonia gas from the discharge valves (at a pressure of between 150 and 180 lbs. per square in.) was passed through an oil separator and then liquified in a 6 pipe condenser (12 feet long), for cooling which from 600 to 900 liters of water were used per hour; from 20 to 40 liters of water per hour were also used for the cooling jacket surrounding the compressor cylinders. The condenser was connected with an ammonia receiver (5 feet long x 10 in. diameter) from which the liquid ammonia was fed at the desired rate through an expansion valve to the cooling coils. The work of cooling was accomplished in 300 feet of expansion piping arranged in 5 coils from which the vaporized ammonia (at a pressure from 5 to 15 lbs. per square in.) was returned to the compressor.

Ventilation. The expansion coils were surrounded by a heavy insulated cooling box, hung from the ceiling of the machine room, through which the air of the laboratory was circulated by means of a small electric fan. The distribution of air was effected through discharge and suction ducts, a supplementary suction duct between the cooling box and outside insuring a constant supply of fresh air. The ducts were provided with numerous adjustable openings for controlling the distribution of air; the suction ducts were also fitted with movable dampers for regulating the delivery of air from the laboratory and outside to the cooling box. The speed of the electric fan was controlled by a regulator; the volume of air delivered from cooling box to laboratory at maximum speed was about 600 cubic feet per minute. The displacement of air from the laboratory by fresh air entering from outside was effected through a damper opening into the hallway from the end of the return duct opposite the cooling box.

Cost of Equipment. The complete cost of the refrigerating equipment as just described was $3,000; $650. for insulation, lumber, and carpenter work, and $2,350 for refrigerating machinery and labor of installation.

WORKING EFFICIENCY OF THE REFRIGERATING EQUIPMENT

The various cycles of heat transference in a system such as just described—from laboratory to circulating air, from circulating air to expansion coils, from expansion coils through vaporized and compressed ammonia to condenser, and from condenser to the cooling water,—are so complex and the difficulty of estimating losses so great that it is possible to make only a very rough calculation of the working efficiency. The variations in outside and inside conditions (sunshine, wind, humidity, persons at work in the laboratory, extent of opening doors, etc.) even in a short period of time present insurmountable obstacles to rigid exactness. The writer has made a large number of comparative measurements under different conditions and without publishing the mass of data at hand will give simply a resume of one or two typical tests.

For a warm summer day at 28°C outside temperature, an expenditure of about 2.9 K.W. hrs. electricity per hour was found to be requisite for maintaining the laboratory at 20°C. The heat units removed per hour by the condenser water were approximately 4500 Cals. and the heat given off to the air of the machine room by electric motor, resistance coils, and compressor estimated at 2500 Cals. per hour.

The large amount of heat given off by motor and compressor shows the importance of isolating all machinery from the laboratory space required to be cooled. Experiments made before the erection of the insulating partition between machine space and laboratory demonstrated the impossiblity of cooling a laboratory satisfactorily on very warm days under such conditions. Working the machine at its fullest capacity there was always a point reached when the radiation from internal and external sources counterbalanced the heat removed by the water. Beyond this point of equilibrium it was impossible to go; the refrigerating machinery was virtually working against itself.

The distribution of the heat removed by the expansion coils in the cooling box was estimated to be as follows:

	Cals. per hour
Cooling air returned from laboratory	2650
" " from outside	550
Freezing moisture from air	815
Heat radiated into cooling box	285
Total heat removed by expansion coils	4300

If the cooling box and ducts could have been placed in the laboratory the item of 285 Cals. radiation would have been saved. Lack of space unfortunately did not permit of the above construction in the equipment at The N. Y. Sugar Trade Laboratory. It is evident, however, from economic reasons that wherever possible in the erection of a constant temperature laboratory the expansion coils, cooling box and ducts should be placed entirely within the insulated walls of the compartment to be cooled.

The average of 2650 Cals. of heat removed per hour from the laboratory is of course very unevenly distributed. In the first two hours of operation the heat removed is largely due to the cooling laboratory materials; in the later hours, when constancy of temperature is being maintained, the removal of heat from radiation is the principal item. The average hourly distribution of the heat removed from the laboratory during 7 hours cooling was roughly estimated to be as follows:

	Cals. per hr.
Removal of heat from cooling laboratory materials	1350
" " " " radiation	653
" " " " persons as work	300
" " " " fan motor	30
	2333
" " " " opening doors etc, (by difference)	317
Total	2650

The ideal system of refrigeration for laboratory purposes is of course that of continuous operation day and night. With an intermittent system, such as the one just described, a certain interval of time must be allowed for saccharimeters, quartz plates and other apparatus to acquire temperature equilibrium. While the air of the laboratory room may be cooled from 26° to 20° in an hour, there is a considerable lag in the cooling of the apparatus and other materials of the laboratory.

It has been found, for example, that a Bates Saccharimeter, which is fitted with a thermometer to indicate the temperature of the quartz wedges, requires about 2½ hours to be cooled from 26° to 20°, when placed in a laboratory of 20° air temperature. This interval may be considerably reduced, however, by cooling the air of the laboratory at first to 19° or 18° and then as soon as the thermometer of the saccharimeter indicates 20° to diminish the speed of the ventilating fan so that the temperature thereafter is kept at exactly the right degree. In The New York Sugar Trade Laboratory from 2 to 3 hours, according to temperature conditions, are allowed for temperature equilibrium before using the saccharimeters. This preliminary interval is of course utilized in weighing out and dissolving the sugars so that no loss of time results from this system of operation.

METHOD OF TEMPERATURE CONTROL

In controlling the temperature of the system just described, the ammonia compressor and ventilating fan are started at 9 A.M. and, if the day is warm, worked at full capacity until the expansion coils in the cooling box are completely covered with frost. As soon as the temperature of the laboratory begins to fall below 20° the speed of the compressor is diminished, the pressure of ammonia in the expansion coils reduced and the ventilating fan slackened. On warm days with an outside temperature exceeding 26° C it is found necessary to run the compressor continuously in order to maintain an equilibrium in the laboratory at 20°. On cooler days with an outside temperature below 26°C, the compressor can be worked intermittently to advantage; sufficient cold can be stored up in the expansion coils to keep the air of the laboratory cool for several hours. By regulating (1) the speed of the compressor. (2) the pressure of ammonia in the cooling coils by means of the expansion valve and (3) the velocity of the ventilating fan, the temperature of the laboratory can be controlled with ease and exactness.

Automatic Control of Temperature. In addition to the above means of controlling temperature, the constant temperature laboratory of The New York Sugar Trade has been firred with an automatic control. The mechanism for this control, which is best adapted for continuous running of the compressor upon moderately warm days, consists of a delicate thermostat which prevents over-cooling of the laboratory by opening a damper which admits warm air from outside.

While the automatic control works with most perfect precision, its usefulness is limited largely to days which have an outside temperature considerably above 20°, otherwise the admittance of outside air is not sufficient to counteract over-cooling. An automatic control which is based upon the admittance of warm outside air is also manifestly less economical than a direct control of the actual work of refrigeration. Owing to the ease with which the temperature can be regulated in the various ways previously described, the automatic control is but little used.

CONDITIONS OF HUMIDITY IN THE CONSTANT TEMPERATURE LABORATORY

At no time in the work of cooling the laboratory has trouble been experienced from condensation of moisture upon walls or apparatus even upon the most humid days. The excess of moisture frozen from the circulating air upon the cooling coils is always sufficient to keep the humidity of the air well below the point of condensation.

COST OF OPERATION

As was stated at the beginning the figures which have been given for the working economy of the cool temperature laboratory were based upon an hourly maintenance at 20° with an outside temperature of 28°. The hourly cost of electricity and water for such maintenance is as follows:

2.9 K. W. hours electricity	@	$.09 =	$0.261
28 Cubic feet water	@	.001 =	.028
Total			$0.289

The cost for lowering the temperature the first hour is greater than this for reasons already explained and is found to average about $0.343. The average hourly cost for cooling the laboratory and maintaining it at 20°C with an outside temperature of 28°C is therefore about $0.30. This figure is considerably above the average cost of operation, however, as the mean outside temperature during summer in New York is much below 28°C. In general the average cost of electricity and water per hour for cooling the laboratory to 20° and maintaining it at this temperature for different outside temperatures was as follows:

Outside Temperature	Running expense per hour for cooling laboratory to 20° C.
30°C	$0.40
28	0.30
26	0.20
24	0.15
22	0.10
20	0.05

The heat from persons at work in the laboratory and from other sources within the building made a small amount of refrigeration necessary even when the outside temperature was 20°.

The annual cost of cooling the constant temperature room of the New York Sugar Trade Laboratory for 7 hours daily during 105 days, has been about $130. for electricity and $20. for condenser water. To this must be added the expense for repairs, interest and depreciation, which are placed at $50. thus making a total running expense of $200. per year. This must be regarded as a small item when the importance is considered of placing as accurate a valuation as possible upon importations of raw cane sugar which for the year exceed $200,000,000 in value.

A number of chemists operating small laboratories have raised the question whether it is not possible to correct the variations in polarizations due to temperature changes by means of suitable formulae or tables, and thus avoid the cost of an expensive refrigerating installation.

As pointed out by the writer in a paper presented at the London Meeting of the International Congress of Applied Chemistry, the employment of temperature corrections based upon changes in the specific rotation of sucrose is accurate only in the case of refined sugars. The argument has been made that since 90 per cent of the imported raw cane sugar polarizes above 95, the sucrose correction factor is sufficiently accurate in most cases. The error in using this factor upon the higher grade Java, Hawaiian, and Peruvian sugars is, to be sure, generally so small as not to be detected by the ordinary saccharimeter. This slight error is nevertheless always in one direction and a constant minus difference of even 0.01 of a saccharimeter degree shows itself invariably in a long average.

The point which has most to be considered, however, is the influence of temperature upon polarizations of the sugars arriving in the hot months of June, July and August, when the errors of correction are naturally the greatest. The greater part of the Philippine sugars, which polarize between 80 and 88, and most of the molasses sugars which polarize below 90, arrive during the summer. These sugars owing to the compensating influence of the large amount of invert sugar which they contain, undergo but little change in polarization with increase in temperature, so that the addition of a correction for the temperature coefficient of sucrose introduces a considerable error.

In the paper presented by the writer at the London Congress of Applied Chemistry it was shown that the temperature coefficients for the polarizations of raw cane sugars tended to fall upon a straight line which extended from a polarization of 100 sugar degrees when the temperature coefficient had a maximum value of 0.003 to a polarization of 80 sugar degrees where the temperature coefficient was zero. By continuing this line, it is seen that with raw cane sugars polarizing below 80 sugar degrees the temperature coefficient becomes a positive quantity, the polarization increasing with rise of temperature instead of diminishing as is the case with pure sucrose.

This same fact was also very clearly shown by Wiley and Bryan, who have published comparative polarizations of various raw cane sugars at different temperatures. Other observers have noted similar effects and the necessary consequence of these results from the opposing influence of temperature upon the specific rotations of sucrose and invert sugar is so self-evident that experimental demonstration might be considered almost superfluous.

During the past summer the writer has made further comparisons upon different grades of cane sugar, one set of polarizations being made in the constant temperature laboratory at 20° and a second set in a laboratory at ordinary temperature, the latter varying between 26° and 30°. In order to fill out certain gaps in the range of sugars examined in 1909, three types of sugar were selected, one type polarizing about 95, a second type about 90, and a third type about 85. The average temperature corrections of these sugars are grouped in the following table together with those of the other cane sugars published in the writer's previous paper.

Series	Number of Sugars Averaged	Average Polarization	Temperature Correction observed for 1° C. increase	Temperature Correction calculated by formula 0.0015 (P −80)	Sucrose Temperature Correction calculated by formula 0.003 P
Old	9	97.14	+0.0287	+0.0257	+0.0291
New	7	95.20	+0.0198	+0.0228	+0.0286
Old	6	92.72	+0.0168	+0.0191	+0.0278
New	6	89.97	+0.0122	+0.0150	+0.0270
Old	10	87.76	+0.0119	+0.0116	+0.0263
New	5	85.61	+0.0074	+0.0084	+0.0257
Old	6	82.80	+0.0051	+0.0042	+0.0248
Old	4	76.18	−0.0051	−0.0057	+0.0229

It is seen that the error in applying a sucrose temperature correction to the polarization of low grade sugars is very pronounced. The average temperature corrections for the different classes of sugars is expressed very closely by the quantity .0015 (P—80), so that the polarization of the average raw cane sugar at 20° when taken at t° may be written

$P^{20} = P^{t} + 0.0015\ (P—80)\ (t^{\circ}—20^{\circ})$

The writer has recommended the use of this formula to chemists who do not have the necessary equipment for making polarizations at constant temperature, always, however, with the caution that this correction formula does not give accurate results for individual samples, whose composition differs from the average type of a given polarization such for example as damaged sugars or sugars abnormally high in moisture or invert sugar.

This constitutes in the writer's opinion the great objection against any system of temperature corrections. Obviously a true correction may be found by making a complete analysis of the product and adding together the temperature coefficients for the percentages of each optically active ingredient present. This, however, is impossible where prompt returns are required upon a large number of samples.

Where large numbers of sugars are examined the constant temperature laboratory is the simplest and only accurate means of solving a most perplexing problem. Movements are now being made to establish such laboratories in Cuba, Louisiana, and Formosa, and it seems safe to predict that sooner or later all important sugar testing laboratories will be thus equipped.

SOUR CANE IN LOUISIANA

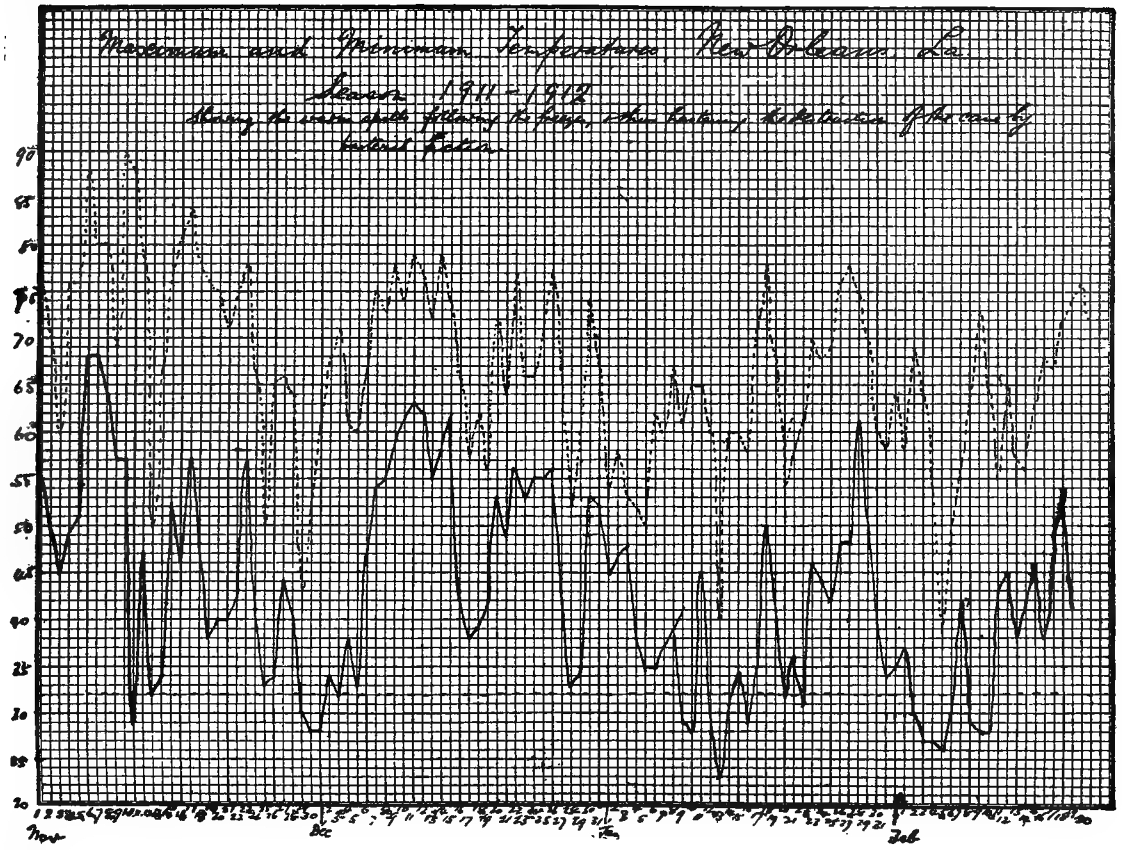
Wm. E. Cross

The geographical position of Louisiana, without any protecting mountains on the north and west and with the warm waters of the Gulf of Mexico immediately to the south, makes the winter climate of a very changeable nature. Periods of warm, oppressively humid weather are not uncommon in November and December, and these often alternate with spells of dry cold, where the temperature is sometimes below freezing point. The following curve of maximum and minimum temperature during the winter 1911–12 will illustrate this.

The effect of these temperature changes upon standing cane can easily be imagined. Cane killed by a freeze, which would still remain "sweet" if the freeze—or even cool weather—were to continue, quickly becomes soured during the warm spells which usually succeed the cold snap.

It is therefore the custom among planters in Louisiana to windrow their cane immediately before a predicted freeze, if possible, and in every case after a bud-killing freeze. Windrowing consists in cutting down the cane with all its foliage and throwing it in the middles between the rows, in such manner that the tops with the leaves, shall completely cover the butts of that previously placed. When the operation is properly conducted nothing should be seen but the leaves of the cane, extending the entire length of the row. Soil may also be thrown over the cane, thus affording further protection against frost, etc.

In a normal winter very little loss may be anticipated from adverse climatic conditions, the grinding season being usually over by the end of December, and most of the unworked cane windrowed some weeks before then. On the other hand, if a freeze comes early in the grinding season it usually inflicts serious loss on the industry. This is because the amount of unworked cane is then so large that even when the mill is stopped and all hands set to work windrowing it is often impossible to


Maximum and Minimum Temperature New Orleans La.
Season 1911–1912
Showing the warm spells following the freeze, often hastening deterioration of the cane by bacterial action.
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
Nov
Dec
Jan
Feb

save any reasonable percentage of the crop. It has been proposed to windrow all the crop before grinding is begun, but this is obviously undesirable: for windrowed cane usually deteriorates slowly but surely, while standing cane, until the freeze comes, increases in sucrose content and in the purity of the juice. Indeed, in the early part of the grinding season (end of October) the cane is often so immature that it is ground almost at a loss by the central factories.

It is thus seen to be almost inevitable, in certain years, that a portion of the planters crop be frozen, and therefore the problem of properly manipulating this sour cane is a serious and pressing one. Of course the cane may be damaged to a greater or less extent. A mature cane can withstand cold far better than an immature or green cane. Again a slight bud-killing freeze might not be followed by any serious souring, while after a severe "splitting" freeze the cane would be very seriously fermented by a few hours of warm weather.

The kind of fermentation which the dead cane undergoes is also of great importance. In some years and localities, the dextran-forming organisms are particularly active; at other times and in other places an acid fermentation (by which mainly acetic acid is produced) predominates; in still other canes an alcoholic fermentation is the one most noticeable. While of course the first and possibly most serious loss is due to the direct destruction of the sucrose, the loss due to the melassagenic properties of the products of fermentation is also a serious one. This secondary loss is also a varying one, dextran being the most melassagenic product of fermentation, and alcohol the least.

The effect of these products of fermentation during the sugar making process might perhaps next be considered. If the juice contains dextran, it is gummy as it comes from the mill; it makes a cloudy "clarified juice," and boils only slowly and with difficulty in the effects, and especially in the vacuum pan. Any appreciable percentage of dextran makes reboiling impossible, besides reducing the yield on first boiling to a considerable extent. Such gummy molasses therefore are consigned to the hot-room. It is an interesting fact, which has not yet been scientifically followed up, that such dextranous molasses usually loses its gummy nature during the six or eight months in the hot-room, reasonably good yields of sugar being obtained, while the gum appears to be broken down by fermentation or other action.

If the fermentation has yielded acid mainly, the juice is more easily workable. It is, however, a fact, that the acids most commonly produced by fermentation give salts with lime which are soluble and highly melassagenic. It is therefore customary to neutralize the juice partly with carbonate of soda (the sodium salts of the acids of fermentation being less melassagenic than those of lime), using only sufficient lime to effect clarification and removal of impurities, etc.

An acid fermented juice of this kind, treated in this way will often give yields of sugar almost as high as unfermented juices of the same sucrose content and purity, showing the melassagenic effect of the sodium salts to be fairly small.

This applies of course to juices which are slightly fermented. A badly fermented juice cannot be worked at all. The question therefore arises, at what stage of fermentation should the cane be rejected. This is a problem of vital importance to the Louisiana industry, where so many large central factories purchase their cane at so much per ton from surrounding planters and farmers.

It is no straightforward matter to judge to what extent cane is fermented, and many mistakes have been made and some injustice done to farmers by central factories in rejecting cane which was really workable. One method of valuing was based entirely on the "acidity test." Cane of more than a certain acidity[1] (say 3cc) was rejected, on the grounds that it was too sour for use. This method was entirely wrong, however, insofar that no consideration was made as to the nature of the fermentation process, or of the degree of maturity of the original cane. Regarding the first factor mentioned, we have seen that a mainly acid fermentation would have less serious effects on the juice than a mainly dextranous one, though the former would indicate a higher "acidity" than the latter. Then, again, a mature cane may be fermented to a further extent than an immature one, without being made useless for the factory.

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[1] "Acidity" is reckoned in Louisiana in the following way: 10 ccs of the juice are titrated against decinormal alkali and the number of ccs required is called the "ccs acidity" of the juice.

The best way to judge sour cane, is therefore to take cognizance of the present state of the cane with regard to sucrose content, purity, etc., as well as taking a measure of the acidity and also, if possible, the gum content. In Louisiana it is the custom to accept canes with purities down to 65, but it is recognized as a losing proposition to attempt to work up juices of much lower purity. The same consideration should be applied to sour canes, remembering the melassagenic influence of the product of fermentation, which would make the minimum purity accepted slightly higher than with fresh cane. The injustice of the "acidity" method of judging cane may be seen from the following two cases. A cane had an acidity of 3.8 cc, i. e., too high to be accepted on the acidity basis. Yet the juice contained 9.25% sucrose and had a purity of 72.95, and, moreover, contained little or no dextran. Another cane had an acidity of only 2.4 ccs, and yet the juice had a sucrose content no higher than 7.36, with a purity of 65.83. A glance at the following table will show further how unreliable "acidity" data alone would be in judging the suitability or otherwise of cane for grinding. From the table can also be seen that consideration of sucrose content, purity, and acidity would give a reasonably good idea of the quality of the cane.

TABLE

(Daily analyses of consignments of cane received by a Louisiana factory; arranged according to acidity)[1]

Below 1.5cc acidity			*1.5–2.0cc acidity*			*2.0–2.5cc acidity*		
s.	p.	ac.	s.	p.	ac.	s.	p.	ac.
13.18	84.52	1.0	11.23	79.38	1.8	9.99	77.37	2.4
10.96	73.60	0.6	9.15	74.07	2.0	10.11	73.02	2.4
11.51	78.11	1.0	11.06	79.07	1.8	11.20	80.41	2.5
10.53	76.26	1.2	8.68	70.97	2.1	9.64	80.50	2.2
11.28	77.90	1.4	8.32	72.05	1.8	9.18	69.89	2.2
9.32	73.51	1.5	8.32	72.05	1.8	7.57	66.08	2.4
8.60	79.85	0.2	8.69	70.72	2.0	8.51	69.62	2.5
8.98	71.71	1.4	8.00	67.82	1.8	7.02	67.59	2.1
8.65	69.94	1.2	10.82	77.10	1.9	11.71	80.23	2.3
			8.17	77.17	1.7	12.14	79.86	2.2
			6.04	62.00	2.0	7.43	67.00	2.4
			11.64	79.74	1.8	12.43	82.90	2.2
			6.78	65.39	2.0	10.42	77.43	2.1
			12.78	83.55	1.8	10.31	75.38	2.1
			12.91	83.47	2.0	10.09	76.06	2.1
			9.83	71.93	1.6	9.59	77.79	2.4
			9.74	73.52	2.1	8.88	74.03	2.4
			9.77	75.33	2.0	7.88	75.36	2.3
			9.96	75.20	2.0	8.92	72.89	2.5
			7.63	69.21	1.8	9.70	77.36	2.4
			8.31	74.68	1.9	9.12	76.97	2.3
			8.75	77.10	2.0	8.87	76.40	2.3
			7.89	70.03	1.9	9.66	69.01	2.4
			8.21	73.05	2.2	9.36	76.00	2.4
			9.13	74.15	1.6	8.89	74.52	2.3
			8.98	78.86	1.8	8.72	75.69	2.2
			11.52	81.40	1.8	8.47	72.10	2.4
			7.96	69.07	1.8	7.36	65.83	2.4
			9.47	72.48	1.9	8.72	69.62	2.5
			8.45	71.49	2.0	10.18	75.10	2.3

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[1] Through the courtesy of Mr. S. G. Chiquelin.

2.5–3.0cc acidity			*2.0–3.5cc acidity*			*3.5–4 0cc. acidity*		
s.	p.	ac.	s.	p.	ac.	s.	p.	ac.
9.96	74.59	2.6	8.30	70.09	3.1	8.86	69.08	3.6
9.97	72.69	3.0	8.05	67.37	3.5	7.75	58.30	4.0
9.31	76.58	3.0	8.40	69.45	3.1	6.94	59.65	4.7
8.47	72.39	3.0	8.42	71.19	3.1	8.51	61.79	3.5
9.94	75.31	2.6	9.07	70.75	3.2	9.25	72.95	3.8
6.26	63.01	2.6	9.18	72.09	3.1	9.95	70.37	3.7
6.86	60.38	2.6	8.36	68.71	3.4	9.20	71.52	4.4
6.92	64.87	2.8	7.62	72.11	3.2			
7.30	66.07	3.0	8.99	59.60	3.0			
8.31	70.32	2.6	8.46	70.90	3.0			
9.56	74.50	2.6	11.08	79.05	3.0			
10.53	78.21	2.6	9.93	78.06	3.0			
7.27	67.46	2.8	8.06	68.15	3.2			
9.24	73.58	2.6	8.84	69.57	3.5			
8.99	73.56	2.8						
9.01	70.50	2.6						
7.73	67.78	2.6						
10.21	75.52	2.8						
9.00	70.21	3.0						
9.13	73.97	2.6						
8.27	69.70	2.5						
9.02	74.70	2.7						
7.67	70.57	2.6						
8.43	69.68	2.8						
7.55	72.60	2.8						
8.63	72.10	2.7						
8.90	74.30	2.8						
9.84	74.30	2.7						
8.84	69.20	2.4						
7.74	71.86	2.9						

A further problem that is presented by sour juices is the reliability or otherwise of the polarization results. The presence of dextran will give false, enhanced sucrose values, and purities; indeed apparent purities of 100 or over have been obtained on fermented juices. If the presence of gum is suspected in the juice it is desirable to clarify in analysis by the alcohol method. The method suggested by Pellet works well: 50 cc juice are taken and clarified with 5 cc lead subacetate solution (or more) and filled up to 100 cc with 95% alcohol.

The last question to be touched upon is the most difficult: the problem of buying and selling sour cane. In Louisiana cane is sometimes sold on sucrose test, most often on the other hand at so much per ton irrespective of sucrose quality. In the contracts, however,—which are almost always made before the season commences—the stipulation is made that the cane must be "sound." Just what "sound" means in this connection is now a question before the courts. It would obviously be unfair to reject cane absolutely because it was very slightly fermented, and on the other hand the mill cannot be expected to pay full prices for sour cane. The expedients adopted during the past season were varied. Some factories gave full prices for cane below 3 cc acidity and rejected that of higher acidity; others took all the cane offered them—with the exception of that which was absolutely valueless, say of purity of 60 and under, and paid a percentage of the sound cane price, this modified value being fixed either arbitrarily or on the basis of the amount of sugar actually obtained per ton, compared with that normally obtained in that particular factory. No universal system has yet however been devised or adopted.

The souring of cane is thus seen to present many problems of a serious and interesting nature. The fact that it is but rarely that any serious portion of the Louisiana crop is damaged by frost probably accounts for the condition that up to now the problems are still far from a satisfactory solution.

(Abstract)

DETERMINATION OF SUCROSE IN CONFECTIONERY CONTAINING COOKED STARCH AND IN MARSHMALLOWS

CHARLES C. ROBERTS

The writer refers to the difficulty encountered in clarifying and filtering solutions of starch paste confectionery and marshmallows.

After describing in detail the experimental work upon which the method is based, he recommends that a dilute alcohol made by diluting 400 c.c. of commercial alcohol to 1000 c.c. with water be used as a solvent. A normal weight (26.048 grams for S&H saccharimeter) of the carefully taken sample of confectionery is dissolved in the above dilute alcohol, transferred with the same solvent to a 200c.c. flask, clarified with sub-acetate of lead solution (Sp. Gr. 1.25), or alumina cream, or both, made to volume with dilute alcohol, filtered on a covered filter with the funnel resting on the receiving cylinder. The filtrate is polarized in the usual manner.

Fifty c.c. of filtrate is evaporated in covered beakers until no odor of alcohol can be detected, then inverted by any recognized method.

Sucrose is calculated by Clerget's formula. The author claims the method to be accurate, rapid, and easy of manipulation.

LE SUCRE CLERGET DES MÉLASSES NORMALES DE BETTERAVES PAR DOUBLE POLARISATION NEUTRE

MR. E. SALLARD
Paris, France

Au point de vue général, la mélasse peut être considérée comme renfermant dans sa matière sèche:

1° Des matières organiques qui sont surtout formées de matières azotées;

2° De sels minéraux ou de sels organiques à base de potasse de soude et souvent de chaux (chlorures, nitrates, sulfates, sulfites, lactates, acétates, butyrates, etc.);

3° De matières de nature pectique qui dégagent du furfurol quand on les chauffe, dans un bain à 150° (avec l'aide chlorhydrique à 12%) (Celles-ci n'entrent dans la mélasse que suivant une proportion insignifiante);

4° etc. Je ne rappellerai que quelques données bibliographiques qui se rapportent aux matières azotées. Ce sont d'ailleurs les matières azotées qui constituent l'objet principal de ce travail.

Pour plus amples details voir le travail de M. Smolenski (Zeitschrift d'autriche, 1911).

Parmi les matières azotées qui existent dans la betterave ou la mélasse et qui ont un pouvoir rotatoire, on peut citer surtout l'asparagine, l'acide aspartique, la glutamine, l'acide glumatique, etc.

L'asparagine a été signalée dans les jus de betteraves par Rossignon en 1842 (V. Comptes-rendus de l'Académie des Sciences).

Pasteur a, le premier, fixé le pouvoir rotatoire de l'asparagine et de l'acide aspartique, dans un travail remarquable et fort étendu qui a été publié en 1851 (Voir "*Annales de physique et de chimie*"). Dans ce travail, Pasteur montre que l'asparagine et l'acide aspartique ont un pouvoir rotatoire lévogyre (en solution alcalinisée par la potasse, la soude et l'amoniaque.) et que l'amoniaque agit plus, dans ce sens, que la soude. Il montre également que l'asparagine et l'acide aspartique ont un pouvoir detrogyre (spécial pour chaque acide) en présence des acides minéraux (sulfurique, chlorhydrique, azotique) et de l'acide citrique, et que ce dernier a une action moins marquée que les premiers.

Dubrunfaut s'occupe, à son tour, de la question de l'asparagine de la betterave dans une Communication à l'Académie des Sciences (9 Juin 1851) et il montre les erreurs auxquelles sa présence peut donner lieu, quand on pratique l'inversion Clerget.

L'asparagine, dit-il, en substance, a un pouvoir rotatoire lévogyre quand elle se trouve en solution aqueuse ou en solution aqueuse, alcalinisée par la potasse, la soude ou l'ammoniaque. Soumise à l'influence des acides, sa rotation passe à droite, ainsi que l'a observé Pasteur. Elle subit la susdite inversion, au moment même du mélange et il suffit de 1 èquivalent d'acide pour la produire entièrement. Des fractions d'équivalent d'acide ont paru produire des déplacements du plan de polarisation, proportionnels aux quantités d'acide ajoutées.

La rotation a gauche de cette substance, son inversion à droite sous l'influence des acides, actions qui, dans les mêmes conditions, sont exactement inverses de celles du sucre cristallisable, doivent être prises en considération pour le dosage du sucre dans les divers cas où on la rencontre, puisque dans l'inversion, elle a pu faire commettre a ceux qui l'ont employée des erreurs tres considérables.

(V. aussi Saccharimétrie) de l'Abbé Moigno, ouvrage paru en 1867 p. 47.)

Clerget touche à la même question dans une communication à l'Académie des Sciences (14 Juillet 1851). Dans sa brochure de 1852 intitulée "ANALYSE DES SUBSTANCES SACCHARIFERES AU MOYEN DES PROPRIÉTÉS OPTIQUES de LEURS DISSOLUTIONS. EVALUATION DU RENDEMENT INDUSTRIEL" il indique le moyen suivant pour corriger les erreurs que peut causer l'asparagine quand on se sert de la polarisation pour obtenir la richesse saccharine des jus de betteraves.

1° Faire la polarisation du jus de pression, aprés avoir déféqué avec du sous-acétate de plomb; soit 77 la lecture +77°

2° Faire la polarisation du jus inverti acide soit: −23°

3° Faire la polarisation du jus inverti, aprés neutralisation de l'acidité avec de la soude, soit −26°5

Clerget admet que, si on représente par −1 le pouvoir rotatoire lévogyre de l'asparagine; il faut représenter par +3,5 son pouvoir rotatoire dans le jus acidifié pour l'inversion. (En d'autres termes, le premier est les 2–7 du second). Comme la différence des deux lectures à gauche est de 3°,5 (26,5−23=3°5), il en conclut que l'asparagine a diminué la déviation à droite de $\frac{3,5\times2}{7}=1$, et il ajoute 1 à la polarisation directe qui devient alors 78.

Le moyen indiqué par Clerget pour déterminer et corriger l'influence de l'asparagine sur la polarisation directe des jus de pression pouvait paraitre exact, au moment où il a été publié; mais je puis dire maintenant qu'il ne l'est pas.

La différence 3,5 précitée est, en effet, une résultante de quatre actions: action de l'acide chlorhydrique sur le pouvoir rotatoire du sucre inverti et des matières azotées; action du sel marin (NaCl) formé pendant la neutralisation, sur le pouvoir rotatoire du sucre inverti et des matières azotées (Voir plus loin les essais correspondants).

La question soulevée par Clerget en 1852 au sujet des matières azotées du jus de pression de la betterave a été reprise par M. Andřlik en 1907 (v. Zeitschrift de Bohême) pour la mélasse, etc.

Dans son travail, M. Andřlik montre que l'acide chlorhydrique augmente, jusqu'à une certaine limite, à droite, le pouvoir rotatoire de l'acide aspartique et de l'acide glutamique, mais que le sous-acétate de plomb n'agit pas de la même facon sur les deux acides: il rend dextrogyre l'acide aspartique et lévogyre, l'acide glutamique. M. Andřlik montre également que l'urée et la bétaïne peuvent ralentir, voire même empêcher l'inversion du sucre, si la température d'action n'est pas trop élevée.

Et finalement, il propose la méthode suivante pour éviter l'influence des matières azotées actives connues, dans la détermination du sucre Clerget. Elle consiste, en somme, à faire les deux lectures, avant et après inversion, en milieu de même acidité chlorhydrique.

Polarisation directe. Transvaser 52 gr. de mélasse dans un ballon de 200 cc.; déféquer avec 20 cc. de nitrate de plomb en solution (1 kg. de nitrate pour 2 litres d'eau) et 20 cc. de soude (100 gr. de soude en plaque pour 2 litres d'eau) et compléter à 200 cc.; filtrer. (Filtrat K.)

Prendre 50 cc. du filtrat K dans un ballon de 100 cc.; ajouter 49 cc. d'une solution contenant 6cc5 d'acide chlorhydrique à 22° Baumé et 5 gr. d'urée; compléter à 100 cc.; filtrer, polariser soit A la lecture;

Prendre 50 cc. du filtrat K, ajouter 25 cc. d'eau et 6cc5 d'acide chlorhydrique à 22° Baumé et invertir suivant Herzfeld; refroidir; compléter à 100 cc.; filtrer, polariser, soit B la lecture;

$$\text{On a sucre Clerget}—\frac{200(A+B)}{143{,}5-\frac{1}{2}t}$$

M. Andřlik emploie 6cc5 d'acide, au lieu de 5 cc., chiffre prescrit par la méthode Clerget-Herzfeld pour les solutions sucrées pures, parce que l'acide chlorhydrique peut déplacer certains acides moins fixes qui se trouvent dans la mélasse, à l'état de sels, et il cherche à obtenir qu'il zeste 5 cc. d'acide chlorhydrique, à l'état libre, pour faire l'inversion.

Il est à noter que M. Ogilvie dans le travail de comparaison qu'il a fait sur la méthode Andřlik et sur la méthode par l'invertas a employé 5 cc. d'acide chlorhydrique à 22° Baumé pour invertir (suivant Herzfeld) 50 cc. de solution normale de mélasse déféquée, et dont l'excédent éventuel de plomb, passé dans le filtrat, avait été précipité avec de l'acide sulfureux. Pour la raison qui vient d'être indiquée, cette quantité d'acide peut être insuffisante.

Si elle est insuffisante, la polarisation directe acide trouvée par M. Ogilvie est trop faible et l'inversion a peut-être été incomplête.

De toute façon, le sucre Clerget-Andrlik trouvé par M. Ogilvie est douteux; il est probablement trop faible.

* * *

Toujours dans le même travail de 1911 sur l'analyse des mélasses de betteraves (V. Int. Sugar Journal 1911) M. Ogilvie a proposé, en vue d'éliminer l'influence des matières azotées actives sur le Clerget, de remplacer l'acide chlorhydrique par l'acide sulfureux (pour faire la polarisation directe *acide*). Voici la méthode qu'il indique à ce propos, dans "l'International Sugar Journal" 1911:

Transvaser 52 gr, de mélasse dans un ballon de 200 cc., déféquer avec 10 à 15 cc. de sous-acétate à 28–30° Baumé, compléter à 220 cc.; agiter; filtrer, prendre 100 cc. de la solution déféquée précédente; ajouter 10 à 15 cc. de solution saturée d'acide sulfureux et compléter à 200 cc.; ajouter de la pâte de papier, agiter, filtrer, polariser; soit A la polarisation directe *acide.*

Faire l'inversion, suivant la méthode française ou la méthode allemande.

La méthode à l'acide sulfureux indiquée par M. Ogilvie en 1911 ne resemble pas tout à fait à la méthode qu'a décrite M. Pellet dans *le Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie de France* (Année 1890–91 pages 439 et 624 et année 1897–98 pages 524 et 1126).

Elle en diffère, et par le but, et par les moyens.

Le but que poursuit M. Pellet est simplement de précipiter le plomb, passé éventuellement dans le filtrat, pour que l'acide chlorhydrique ajouté reste entièrement à l'état libre et puisse assurer l'inversion complète pendant le chauffage,[1] mais, dans sa publication il n'est pas question des matières azotées de la mélasse, ni de leur influence sur le sucre Clerget.

J'ajouterai que la précaution de précipiter le plomb est inutile avec la quantité d'acide et la durée de chauffage qu'indique M. Pellet (20 à 30 minutes à 70°.) Elle est même inutile quand on pratique la méthode commerciale française (voir ma communication à la Commission de la Raffinose à Berlin Septembre 1910).

[1] La défécation est faite avec du sous-acétate de plomb dont la quantité est proportionnée aux besoins de la mélasse.

Au surplus, l'acide chlorhydrique ajouté ne reste pas entièrment à l'état libre, même quand il n'y a plus de plomb à précipiter. (Voir plus haut.)

Les moyens que recommandent M. Pellet pour pratiquer l'inversion Clerget et précipiter le plomb sont les suivants: (Voir Bull. Assoc. 1890–91 p. 439 et 624).

Prendre 100 cc. de solution de mélasse déféquée et filtrée (25 gr/250 cc.); ajouter lg. 5 de SO^2 sous forme de solution; completer à 200 cc.; filtrer (filtrat K).

Prendre 50 cc. du filtrat K, qui contiennent $\frac{1.5}{4} = 0$ gr. 375 de SO_2;

Ajouter 5 cc. d'eau; polariser; soit A la lecture;

Prendre 50 cc. du filtrat K; ajouter 5 cc. d'HCl à 22° Baumé; invertir en laissant le ballon 20 à 30 minutes dans un bain préalablement porté à 70°. Refroidir. Affleurer à 55 cc.; Polariser.

Si on a un saccharimètre, des ballons et pipettes bien gradués appliquer les formules de Herzfeld:

$$S = \frac{100(A+B)}{142-66-\frac{1}{2}t} \text{ (s'il y a du saccharose et du ``\textit{glucose}'').}$$

$$S = \frac{0{,}5124A - B}{0{,}839} \text{ (s'il y a du saccharose et du raffinose).}$$

Je fais remarquer que les formules de Herzfeld s'appliquent à la méthode d'inversion Clerget-Herzfeld, mais pas à la méthode d'inversion qui vient d'être indiquée. Il y a là une confusion.

En 1897–98 (V. Bull. Asso. 1897–98 p. 524 et 1176) M. Pellet opère de même; mais il part de 100 cc. de solution normale française ou normale allemande déféquée et filtrée.

A 100 cc. de solution normale déféquée et filtrée, il ajoute 10 à 20 cc. de solution sulfureuse à 7 gr. 5 de $SO_2\%$ cc., puis complète à 200 cc. Il prescrit donc 0g. 186 à 0g. 375 de SO_2 pour faire la polarisation directe, contre 2g. 15 de HCl vrai pour faire l'inversion.

Il prescrit de nouveau les formules Herzfeld et fait remarquer ("Bull. Assoc. 1897–98 p. 532) que "pour des instruments de précision, on trouve généralement un coefficient d'inversion se rapprochant de celui dit allemand, soit 142,66 mais que pour d'autres appareils on pourra être amené à faire usage de l'ancien coefficient Clerget 144."

Il y a là une erreur, puisqu'on peut obtenir les deux coefficients avec un même saccharimètre, suivant qu'on emploie la méthode française Clerget ou la méthode allemande. Clerget-Herzfeld.

Je ferai remarquer aussi que les quantités d'acide sulfureux prescrites par M. Ogilvie sont plus importantes que celles indiquées par M. Pellet en 1891 et 1898. M. Ogilvie prescrit en effet:

Methode allemande; 5 cc. à 7cc5 de solution sulfureuse saturée soit: 0gr57 à 0gr75 de SO_2 contre 2gr15 de HCl vrai, au lieu de 0gr 186 à 0gr375, quantités prescrites en 1898.

* * *

Enfin, en étudiant les données de Clerget (1852) nous sommes arrivés à la méthode suivante, qui peut être appliquée aussi bien avec l'inversion française qu'avec l'inversion allemande.

En voici les grandes lignes, si on fait l'inversion proprement dite d'après la méthode allemande:

1° Prendre 50cc de solution normale neutre de mélasse déféquée dont l'éxédent de plomb a été séparé; ajouter Ncc d'une solution de chlorure de sodium ou de potassium pur, apportant en chlorure l'équivalent de l'acide chlorhydrique qui sera employé pour l'inversion; compléter à 100cc, polariser à 20°C: soit A la lecture;

2° Prendre 50cc de la même solution normale; faire l'inversion avec la dose d'acide chlorhydrique nécessaire; refroidir; neutraliser avec de la soude ou de la potasse en solution; refroidir à 20° C, compléter à 100cc; polariser à 20°C; soit B la lecture

D'où sucre Clerget % de mélasse $-\frac{200\ (A+B)}{\text{coeff. d'inversion} - \frac{1}{2}\ t}$

Coefficient d'Inversion—1° Prendre 50cc de solution sucrée pure ayant la même polarisation que la solution normale de mélasse, ajouter N'cc de chlorure de sodium ou de potassium en solution apportant en chlorure l'équivalent de l'acide chlorhydrique employé pour l'inversion, compléter à 100cc, polariser à 20° C, soit A'la lecture.:;

2° Prendre 50cc de la même solution de sucre; ajouter

25cc d'eau et 5cc d'acide chlorhydrique à 22 Bé, invertir, neutraliser avec de la soude ou de la potasse; refroidir à 20°, compléter à 100cc, polariser à 20°: soit B′ la lecture à gauche;

3° Prendre 50cc de la même solution de sucre, compléter à 100 cc avec de l'eau; polariser à 20°, soit A″ la lecture.:

$$\frac{\underline{A''=100\,(A'+B')}}{x-\frac{1}{2}\,t}$$

d'où x=

Nota—Pour faciliter les opérations, on peut avoir des solutions de soude ou de potasse et de chlorure de sodium ou de potassium qui correspondent, sous volume connu, à l'acide chlorhydrique qui sert pour l'inversion.

* * *

Je vais rapporter quelques expériences que nous avons faites et qui permettent d'éclairer ou de discuter ces différentes méthodes.

Parmi les résultats auxquels nous sommes arrivés, il y en a qui sont déjà connus; mais, pour ne pas trop allonger ce travail, j'ai laissé de coté la partie bibliographique.

I—ACTION DES ACIDES ET DES SELS SUR LE SACCHAROSE EN SOLUTION

a. Action des acides

On sait que beaucoup d'acides ont la propriété d'invertir le saccharose, même à froid; mais le pouvoir inversif varie d'un acide à l'autre. C'est ainsi que les acides organiques sont moins actifs que les acides minéraux, et même, dans chaque groupe (minéral ou organique) il y a des différences de l'in à l'autre.

Comme M. Andrlik propose d'acidifier avec de l'acide chlorhydrique le liquide de polarisation directe, nous avons suivi l'action invertive de l'acide chlorhydrique, soit sur les solutions sucrées pures, soit sur les mélasses et masses cuites déféquées, après précipitatión de l'éxcédent éventuel de plomb passé dans le produit déféqué.

Les lectures ont été faites aux températures de 10°,9 à 20°, Voici les résultats qu'elles ont donnés:

	Solution sucrée pure	Masse cuite de 2° jet déféquée	Mélasse déféquée
	5cc d'acide à 22° Be+ urée, pour 100cc de solution	6cc5 d'acide à 22° Baumé + urée, pour 100cc de solution déféquée	6cc5 d'acide à 22° Baumé + urée, pour 100cc de solution déféquée
Sans acide	23,10	23,10	23,10
2 minutes après l'addition de l'acide	22,92	22,10	21,53
4	22,81	22,09	21,50
6	22,75	22,04	21,46
8	22,65	21,95	21,40
10	22,53	21,87	21,36
12	22,48	21,80	21,31
15	22,39	21,68	21,24

b. Action des Sels

Il y a, dans la mélasse, des sels organiques et des sels minéraux à base de potasse, de soude et souvent de chaux.

Si on suit la méthode Andrlik, ces sels se trouvent avant l'inversion, en présence de saccharose et, après l'inversion, en présence de sucre inverti.

Comme la mélasse contient, en moyenne, 5% de potasse et 1% de soude, cela représente, en HCl vrai:

0gr 82 pour 16 gr 26 de mélasse;

0gr 65 pour 13 gr de mélasse;

Soit en chlorure de potassium;:

1 gr. 67 pour 16gr 26 de mélasse

1 gr 32 pour 13 gr. de mélasse.

Ces chiffres n'ont pour but que de fixer les idées.

Voici quelques résultats d'essais qui montrent l'action des sels sur le pouvoir rotatoire du sucre en solution:

	Polarisation	Différences avec le témoin
50cc de solut. sucrée+50cc d'eau.......	39	
50cc “ “ “ +4 gr. de CO_3K_2 ammener à 100cc......	37,85	0,15
50cc “ “ “ +4gr 3 de Kcl id.......	38,7	0,30
50cc “ “ “ +5,68 d'acétate de K_2O..	38,63	0,37
50cc “ “ “ +5gr.04 de SO_4K_2......	38,73	0,27
50cc “ “ “ +3gr. 6 de SO_3Na_2......	38,37	0,63

Avec des doses croissantes de sel marin, les résultats sont les suivants:

50cc de solution sucrée+50cc d'eau.........	38,53	
50cc “ “ “ +4gr. de NaCl compléter à 100cc..	38,22	0.31
50cc “ “ “ +10gr “	37.77	0.76
50cc “ “ “ +12gr “	37.49	1.04
50cc “ “ “ +20gr “	36.79	1.74

II—ACTION DES SELS ET DES ACIDES SUR LE SUCRE INVERTI

1°—*Action des sels*

Une solution de sucre pur a été invertie complètement à l'ébullition par quelques gouttes d'acide chlorhydrique puis neutralisée avec de la soude.

À la solution de sucre inverti, on a ajouté[1] les mêmes sels que ceux qui avaient été employés pour la solution de saccharose. Voici les résultats obtenus:

	Polarisation	Différences avec le témoin
50cc de solution d'inverti+50cc d'eau................	−10,62	
50cc “ “ +4 gr.3 de KCl, compl. à 100cc	−11,35	0,73
50cc “ “ +5g.68 d'acetate de K_2O “	−11,26	0,64
50cc “ “ +7g.4 de lactate de K_2O “	−11,04	0,42
50cc “ “ +4gr. de NaCl “	−12,34	0,72
50cc “ “ +10gr. de NaCl “	−13,41	1,79
50cc “ “ +12gr. de NaCl “	−13,80	2,18
50cc “ “ +20gr. de NaCl “	−15,13	3,51

Comme on le voit, ces sels, augmentent plus la déviations à gauche du sucre inverti qu'ils ne diminuent la déviation à droite du saccharose.

Nous avons refait les mêmes essais avec les mêmes sels, mais en ajoutant une quantité d'acide chlorhydrique suffisante pour faire passer toute la base du sel à l'état de chlorure; on pratiquait ensuite le chauffage Clerget avec 5cc d'acide chlorhydrique libre.

Les résultats obtenus ont été les suivants:

	Avant l'addition de de l'acide		Après l'addition de de l'acide et Chauffage Clerget	
	Polarisasation	Différ. av. le témoin	Polarisasation	Differ. av. l. té.
50cc de solut. d'inverti+50cc d'eau	− 9,94		−10,74	
50cc " " +4gr. de CO_3K_2 compl. 100cc......	−10.79	0,85	−11,26	0,52
50cc " " +4gr. 3 de KCl comp. 100cc......	−10,67	0,73	−11,55	0,81
50cc " " +5gr.68 d'acetate de K_2O id.	−10,54	0,60	−11,16	0,42
50cc " " +7, 4 de lactate de K_2O id.	−10,26	0,32	−11,27	0,53
50cc " " +5,04 de siulfate de K_2O id.	−10,60	0,66	−11,40	0,66
50cc " ' +3,6 de sulfite de N_2O id.	−10,47	0,53	−11,18	0,44

Pour savoir si la solution d'inverti ne contenait pas de saccharose, on l'a polarisée en présence d'acide chlorhydrique et d'urée, puis après addition d'acide et chauffage Clerget, elle a donné:

Lecture avant chauffage—11°

Lecture après chauffage—10°74

La différence, avant et après inversion, provient de l'action de la chaleur et de l'acide sur le sucre inverti.

Somme toute, ces résultats sont du même ordre que les premiers: ils montrent que les sels additionnés d'acide chlorhydrique ont plus d'action sur le pouvoir rotatoire du sucre inverti que sur celui de saccharose.

2°—*Action des acides sur le sucre inverti*

A une solution de sucre inverti, préparée comme il vient d'être dit, on a ajouté des doses croissantes d'acide chlorhydrique ou d'acide sulfureux. Voici les résultats obtenus:

	Polarisation	Différences av. le Témoin
1°—ADDITIONS DE HCl		
50cc de Solut. d'inverti+50cc d'eau	— 9,8	
50cc " " +5cc d'acide 22° Be compléter 100cc	—10,48	0,68
50cc " " +10cc d'acide "	—11,00	1,2
50cc " " +15cc — "	—11,31	1,51
50cc " " +20cc — "	—11,68	1,88
2°—ADDITIONS DE SO_2		
50cc " " +50cc d'eau	— 9,8	
50cc " " +0g.54 de SO_2 amener	— 9,8	
50cc " " +2,26 de SO_2 à 100cc	— 9,79	
50cc " " +3,55 de SO_2	— 9,79	

Alors que l'acide chlorhydrique, employé sous doses croissantes, augmente la déviation à gauche du sucre inverti, l'acide sulfureux employé sous doses croissantes, reste sans effet.

Si après avoir fait l'inversion Clerget et la lecture à gauche on neutralise avec de la soude, on obtient ensuite, sur le liquid neutre, une déviation à gauche plus accentuée.

Polarisation à gauche (acide)—7,14

Polarisation à gauche (neutre)—7,26

Ces résultats montrent que le chlorure de sodium augmente plus la déviation à gauche du sucre inverti que la quantité équivalentaire d'acide chlorhydrique.

III—ACTION DES ACIDES ET DES SELS SUR LES MATIÈRES AZOTÉES DE LA MÉLASSE

a. Action des Acides

Dans les tableaux qui suivent, l'acide chlorhydrique et l'acide sulfureux sont exprimées en acides vrais, HCl et SO_2 en admettant que:

10 cc. d'acide chlorhydrique à 22° Baumé = 4 gr. 3 de HCl vrai et que 100 cc. de solution saturée sulfureuse à 20° = 10gr. 6 de SO_2.

a. Solution d'asparagine a 17gr. environ par litre

50cc. de solution d'asparagine ont été additionnés de doses croissantes d'acide chlorhydrique ou d'acide sulfureux en solution; puis on a complété à 100cc et on a fait les lectures au polarimètre.

1°—ADDITIONS D'ACIDE CHLORHYDRIQUE

						Polarisation multipliée par 2
50cc de solution d'asparagine			+50cc d'eau			−0,6
50cc	"	"	+2 g.15 HCl puis compléter à 100cc			+2,82
50cc	"	"	+4 g.3 HCl	"	"	+2,85
50cc	"	"	+6 g.43 HCl	"	"	+2,91
50cc	"	"	+8 g.60 HCl	"	"	+3,01
50cc	"	"	+12 g.9 HCl	"	"	+3,06
50cc	"	"	+21 g.5 HCl	"	"	+3,05

2°—ADDITIONS D'ACIDE SULFUREUX

50cc de solut. d'asparagine			+50cc d'eau			−0,6
50cc	"	"	+1 g.16 SO_2 compléter à 100cc			+2
50cc	"	"	+1 g.88 SO_2	"	"	+2,14
50cc	"	"	+2 g.90 SO_2	"	"	+2,42

b. Solution d'Acide Glutamique

La solution contient environ 15 gr. par litre et on ajoute un peu de soude pour faire la dissolution. Voici les résultats obtenus:

1°—ADDITIONS D'ACIDE CHLORHYDRIQUE

							Polaris.
75cc de solut. d'acide glumatique				+35cc d'eau			−0,26
75cc	"	"	"	+0,60 de HCl amener à 110 cc			+1,33
75cc	"	"	"	+1,29 de HCl	"	"	+1,87
75cc	"	"	"	+2,15 de HCl	"	"	+1,89

2°—ADDITIONS D'ACIDE SULFUREUX

						Polaris.
75cc de solut. d'acide glutamique				+35 cc d'eau		−0,26
75cc	"	"	"	+0g 54 de SO_2 compléter à 110cc		+0,93
75cc	"	"	"	+1gr13 de SO_2	"	+1,46
75cc	"	"	"	+1gr88 "	"	+1,64

En récapitulant l'effet produit par ces doses équivalentaires d'acide chlorhydrique HCl et d'acide sulfureux SO_2, on peut dresser le tableau suivant:

	2 gr 15 d'HCl	1 gr 88 de SO^2
Asparagine	+2,82	+2,14
Acide glutamique	+1,89	+1,64

Bien que les polarisations relatives à l'acide glutamique ne se rapportent pas aux mêmes concentrations que celles relatives à l'asparagine, on voit néanmoins que l'acide chlorhydrique, sous quantités équivalentaires égales, a plus d'action sur le pouvoir rotatoire des matières azotées que l'acide sulfureux.

Voyons maintenant leur action sur la mélasse.

1° *Serie d'essais*

Nous avons suivi la méthode de defecation indiquée par Mr. Ogilvie pour pratiquer l'inversion par l'invertase.

Prendre 26 gr. de mélasse, déféquer avec du sous-acétate; compléter à 100 cc; agiter, filtrer;

Précipiter le plomb avec un courant de gaz SO_2, saturer l'éxcédent de SO_2 avec du carbonate de chaux pur et sec en poudre; ajouter un peu de kieselguhr; filtrer.

	Polarisation×2		
	1° mélasse	2° mélasse	3° mélasse
1° ADDITIONS D'ACIDE CHLOROHYDRIQUE			
50cc de solut. normale déféquée+50cc d'eau	43,48	40,56	43,14
50cc de solut. +0g. 6 de HCl; compléter à 100cc avec de l'eau	44,48		44,02
50cc de solut.+0g 86 de HCl; compléter à 100cc avec de l'eau		42,04	44,36
50cc de solut.+2g 15 de HCl; compléter à 100cc avec de l'eau	45,38		44,64
50cc de solut.+2g 79 de HCl; compléter à 100cc avec de l'eau		42,06	44,70
50cc de solut.+ 4g. 3 de HCl; compléter à 100cc avec de l'eau	45,44	42,07	44,72
50cc de solut.+ 6g45 de HCl; compléter à 100cc avec de l'eau	45,60	42,08	44,72
2° ADDITIONS D'ACIDE SULFUREUX (SO_2)			
50cc de solution+50cc d'eau	43,48	40,56	43,14
50cc de solut,+0gr54 de SO_2; compléter à 100cc avec de l'eau	43,96		43,38
50cc de solut. +0g 80 de SO_2; compléter à 100cc avec de l'eau		40,96	43,78
50cc de solut. +1g. 99 de SO_2; compléter à 100cc avec de l'eau		41,90	
50cc de solut. +2g. 27 de SO_2; compléter à 100cc avec de l'eau	45,20		
50cc de solut. +2g. 45 de SO_2; compléter à 100cc avec de l'eau			44,58
50cc de solut. +2g. 70 de SO_2; compléter à 100cc avec de l'eau			44,68
50cc de solut. +2g. 85 de SO_2; compléter à 100cc avec de l'eau		42,06	
50cc de solut. +3g. 55 de SO_2; compléter à 100cc avec de l'eau	45,30		

2^e^ *Serie d'essais*

Nous avons fait la défécation suivant la marche indiquée par M. Ogilvie pour la méthode à l'acide sulfureux.

Transvaser 52gr. de mélasse dans un ballon de 200cc; déféquer avec 10 à 15 cc de sous-acétate; compléter à 200 cc (au lieu de 220cc); filtrer;

A 50cc de cette solution normale, ajouter des doses croissantes d'acide chlorhydrique ou d'acide sulfureux.

	Polarisation×2	
	1° Mélasse	2° Mélasse
1°—ADDITIONS D'ACIDE CHLORHYDRIQUE		
50cc de solution de mélasse+50cc d'eau	40,68	45,06
50cc de solut. + 0g60 de HCl vrai; compléter à 100	41,44	46,04
50cc de solut. + 0g90 de HCl. vrai; completer à 100cc	42,00	46,08
50cc de solut. +2g15 " " " " "	42,06	46,14
50cc de solut. + 2g58 " " " " "	42,10	46,11
50cc de solut.+ 3g87 " " " " "	42,06	
2°—ADDITIONS D'ACIDE SULFUREUX (SO_2)		
50cc de solution de mélasse+50cc d'eau	40,68	45,06
50cc de solut. +0g. 54 de SO_2; compléter à 100cc	41,38	45,42
50cc de solut. +0g. 80 " " "	41,72	45,80
50cc " " + 1g.88 " " "	42,44	"
50cc " " +2g. 26 " " "	42,56	46,20
50cc " " +3g. 4 " " "	42,64	"

Comme on le voit, par les chiffres qui précèdent, les quantités d'acide sulfureux qui sont nécessaires pour donner la même polarisation directe que 5 cc d'acide chlorhydrique à 22° Baumé (soit 2gr. 15 de HCl) ou 6 cc 5 d'acide à 22° Baumé (soit 2 gr. 79 de HCl vrai), sont variables, d'une mélasse à l'autre.

Ainsi, pour la première mélasse déféquée (sans plomb) il faudrait environ 3 gr. 55 de SO_2 pour produire le même effet que 5cc d'acide chlorhydrique à 22° Baumé; mais il n'en faudrait que 2gr. 85 environ pour la deuxième mélasse.

Et ces quantités sont supérieures à celles que prescrit M. Ogilvie et supérieures à celles qui sont prescrites en 1891 et 1898 par M. Pellet.

On ne peut donc indiquer, une fois pour toutes, les quantités d'acide sulfureux qui donneront la même polarisation directe que l'acide chlorhydrique employé pour l'inversion. Ces quantités varient d'une mélasse à l'autre.

b. Action des sels sur les matières azotées

1°—SOLUTION D'ASPARAGINE À ENVIRON 17 GR. PAR LITRE

Solutions A	Polarisation
75cc de solut. d'asparagine+25 cc d'eau	+0,31
75cc " " + 4 gr de CO_3K_2; compléter à 100cc	+0,30
75cc de solut. d'asparagine+4 g.3 de KCl; compl. à 100cc	+0,10
75cc " " +5 g68 acetate de K_2O "	+0,095
75cc " " +7g. 4 lactate – "	+0,01
75cc " " +5g04 SO_4K_2 "	+0,18
75cc " " +5g04 SO_3Na_2 "	+0,15

2°—SOLUTION D'ASPARAGINE À ENVIRON 18 GR. PAR LITRE

Solutions B	Polarisation
75cc de solut. d'asparagine+25 cc d'eau	−0,32
75cc de solut. " +2gr. Na Cl; compl à 100cc	−0,08
75cc " " +2 g 5 NaCl; "	0
75cc " " +5 gr NaCl; "	+0,19
75cc " " +10gr NaCl "	+0,47
75cc " " +15gr. NaCl "	+0,67

3° Les solutions d'asparagine et de sels ont été additionnées d'acide chlorhydrique (5cc en plus de la dose nécessaire pour saturer les bases) puis chauffées suivant Clerget et polarisées. Voici les résultats obtenus:

1°—Solutions A	Polarisations ramenées à la même dilution
50cc de solution A+5cc HCl	+2,36
50cc " avec CO_3K_2+7cc 5 HCl à 22° Baumé	+2,40
50cc " " KCl+5ccHCl "	+2,43
50cc " " l'acétate de K_2O+7cc, 5 HCl "	+2,41
50cc " " lactate de K_2O+7cc5 HCl "	+2,42
50cc " " SO_4K_2+5cc HCl "	+2,40
50cc " " SO_3Na_2+7cc, 5 HCl "	+2,40

Si on fait les lectures, après addition d'acide, mais sans chauffage, les polatisations à droite sont les mêmes: soit 2,40 environ contre 2,36.

Cela revient à dire aue l'action de l'acide couvre à peu près l'action des sels.

Il en est de même pour les solutions d'asparagine qui ont recu du NaCl.

2°—SOLUTIONS B

2° Solutions B	Polarisations
50cc de solution B+5 cc HCl à 22° Baumé (sans chauffage)	+2,10
50cc " à 2 gr. de NaCl+5 cc HCl à 22° Baumé	+2,12
50cc " à 5 gr. de NaCl+5 cc HCl à " "	+2,14
50cc " à 10 gr. de NaCl+5 cc HCl à " "	+2,16
50cc " à 15 gr. de NaCl+5 cc HCl à " "	+2,17

Voici quelques résultats que nous avons obtenus en pratiquant:

1° la méthode de double polarisation acide (Andrlik);

2° la méthode Ogilvie (par l'invertase)[1] (V Int. Sugar Journal 1911)

3° la méthode de double polarisation neutre (Saillard)

et en faisant l'inversion chimique proprement dite, d'après la méthode Clerget-Herzfeld.

Pour chaque méthode, on a fait l'inversion sur 50cc de solution normale de mélasse déféquée et après séparation de l'excédent éventuel de plomb passé dans le filtrat, au moyen d'acide sulfureux (qui décolore) ou d'acide oxalique ou d'acide carbonique. (Les oxalate et carbonate de plomb sont un peu solubles; mais cela n'a qu'une influence insignifiante sur le résultat de l'inversion chimique.)

L'inversion chimique était faite avec 5cc d'acide pour les solutions sucrées pures et avec 6cc 5 pour les mélasses. Les ballons restaient dans le bain à 70°, 5 minutes, à compter du moment où le contenu du ballon accusait 69°.

Les coefficients d'inversion ont été etablis en partant de solutions sucrées pures donnant les mêmes polarisations que la mélasse déféquée.

C'est Berthelot qui, le premier, a montré que la levure de bière secréte un ferment soluble qui invertit le sucre sans en provoquer la fermentation. (C. R. 1860)

1° COEFFICIENTS D'INVERSION

	Pour la double polarisation neutre (Saillard) (V. page 8)	Pour la double polarisation Andrlik		Pour la méthode à l'invertine (Ogilvie)
		Avec les deux lectures acides	Avec la polarisation directe (neutre) et la deviation à gauche (acide)	
1°........	141.94	141.18	142.06	
2°........	141.96	141.32	142.12	
3°........	141.93	141.12	142.10	141.18
4°........	141.96	141.24	142.23	141.05
5°........	141.92	141.37	142.25	141.21
6°........	142.07	141.42	142.28	141.07
7°........	142.12	141.41	142.21	141.20
8°........	142.13	141.40	142.25	141.11
Moyennes.	142.00	141.30	142.19	141.13

NOTA—Les coefficients d'inversion varient plus, d'un essai à l'autre, quand on les établit avec les deux polarisations acides; on en voit la raison.

ANALYSES DES MELASSES[1]

Mélasses	Polarisation directe		Polarisation directe Ogilvie
	Polarisation neutre Saillard (V page 8)	Polarisation directe Acide Andrlik	
1	44.14	46.10	44.4
2	47.04	49.00	47.28
3	40.16	41.92	40.46
4	42.30	44.20	42.58
5	42.42	44.30	42.72
6	40.14	42.02	"
7	41.88	43.94	"

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[1] Chaque essai a été fait en double et on a pris la moyenne des résultats.

SUCRE CLERGET

Mélasses	Par double polarisation (neutre) (Saillard)	Double polarisation acide (Andrlik) avec coefficient d'inversion relatif aux 2 lectures acides	Méthode Ogilvie par l'invertase
I	46.66	46.32	46.32
2	48.86	48.68	48.68
3	42.16	41.90	41.83
4	44.80	44.35	44.26
5	44.52	44.23	44.18
6	42.10	41.90	41.90
7	44.34	43.98	43.98

MÉLASSES DE 1911–12. COMPARÉES À CELLES DE 1910–11

Il est maintenant bien établi que la méthode Clerget commerciale française, de même d'ailleurs que la méthode Clerget commerciale allemande, donnent un sucre Clerget trop faible, surtout avec les mélasses qui ont une forte teneur en azote, comme cela arrive le plus souvent dans les années sèches.

A titre d'indication, je vais citer les résultats moyens que nous avons obtenus en comparant les mélasses de 20 Usines françaises en 1910–11 et en 1911–12. Les 20 usines ont été les mêmes pour les deux campagnes.

Le Clerget ordinaire a été établi suivant la méthode commerciale française qui est la suivante:

Prendre 32gr. 6 de mélasse neutre dans un ballon de 200cc; déféquer avec 20cc de sous-acétate à 28°–30° Baumé; compléter à 200cc, filtrer, polariser (Filtrat K): soit A la polarisation directe;

Prendre 50cc du filtrat, ajouter 5cc d'acide chlorhydrique à 22° Baumé; porter le ballon à 68–70° en 10 ou 12 minutes; extraire le ballon du bain et le laisser refroidir spontanément à l'air jusqu'à 40°, puis dans un courant d'eau, jusqu'à 20°. Affleurer à 55cc avec de l'eau. Filtrer, polariser: soit B la lecture rapportée à 100cc du filtrat.

$$\text{Sucre Clerget} = \frac{100(A+B)}{144-\frac{1}{2}t}$$

Pour faire la polarisation directe acide, prendre 50cc du filtrat. Ajouter 10cc d'une solution contenant 5cc d'acide chlorhydrique et de l'urée; ajuster au trait 60cc, filtrer, polariser, soit:

A′ la lecture ramenée à la solution normale

$$\text{d'ou Sucre Clerget acide} = \frac{100(A'+B)}{144-\frac{1}{2}t}$$

Il est vrai que le coefficient d'inversion 144 se rapporte à la solution normale du sucre pur et que la mélasse ne contient qu'environ 50% de sucre; mais il s'agit là d'une méthode conventionnelle.

D'ailleurs, il n'est pas bien certain que les coefficients d'inversion à employer pour la mélasse sont forcément les mêmes que pour les solutions sucrées pures de méme teneur en sucre. Il faut tenir compte, en effet, de l'influence des sels de la mélasse (Voir plus haut)

J'ajoute que les 5cc d'acide ajoutés, pour l'inversion, suffisent, dans le cas présent, pour assurer l'inversion complète pendant la durée de chauffage et de refroidissement (V. Circ. held. 1908) *i*

Voici donc les résultats moyens qui se rapportent aux mélasses de 20 usines françaises pendant les deux dernières campagnes:

	Campagne 1910–11	Campagne 1911–12
Azote total pour 100 de matière seche	2	2.62
Polarisation directe ordinaire % de mélasse	47,41	47,73
Polarisation directe acide id	48,41	49,62
Sucre Clerget ordinaire id	46,23	47,14
Sucre Clerget (double lecture acide) id	46,96	48,57
Différence entre le Clerget acide et le Clerget ordinaire.	0,73	1,43
Différence entre la polarisation directe acide et la polarisation directe ordinaire	1,00	1,89

Si on faisait intervenir les coefficients d'inversion qui se rapportent aux solutions sucrées pures, de même teneur en sucre, le sucre Clerget ne se trouverait modifié que légèrement et les différences (Sucre Clerget acide—Sucre Clerget ordinaire) resteraient sensiblement les mêmes.

Je note, en passant, que le Clerget acide des mélasses de 1911–12 a été, en moyenne, supérieur à la polarisation directe ordinaire, alore que, pour la campagne 1910–11, on remarque le contraire (il s'agit de résultats moyens se rapportant à 20 usines).

EN RESUMÉ

1°—Les sels les plus courants de la mélasse de betteraves diminuent moins la déviation à droite du saccharose qu'ils n'augmentent la déviation à gauche du sucre inverti correspondant.

Il semble donc difficile de déterminer le sucre Clerget exact des mélasses de betteraves (dans l'état actuel de nos connaissances).

2°—L'acide chlorhydrique augmente la déviation à gauche du sucre inverti; mais l'acide sulfureux est sans action sur elle;

3°—Les sels courants de la mélasse ont une action sur le pouvoir rotatoire des matières azotées actives de la mélasse ils le font passer de gauche à droite. Une fois la déviation à droite réalisée, elle augmente jusqu'a une certaine limite, si on augmente la dose de sels et l'action varie d'un sel à l'autre.

Ajoute-t-on de l'acide chlorhydrique à la solution de matières azotées (acide glutamique, asparagine) et de sels? Les rotations à droite deviennent sensiblement égales (pour les doses essayées).

4°—Sous quantités équivalentaires égales, l'acide chlorhydrique augmente plus le pouvoir rotatoire à droite de l'asparagine, de l'acide glutamique, que l'acide sulfureux.

5°—L'acide chlorhydrique employé pour la polarisation directe des solutions sucrées pures produit toujours une diminution de la lecture, même s'il est mélangé avec de l'urée et si on fait la lecture, même s'il est mélangé avec de l'urée, et si on fait le lecture en 2 ou 3 minutes. L'acide sulfureux n'invertit pas le sucre pendant le temps que dure la polarisation directe à 20°; mais on ne peut indiquer, une fois pour toutes, les quantités d'acide sulfureux qui donnent, avec les mélasses, la même déviation à droite que l'acide chlorhydrique employé pour l'inversion Cette quantité peut varier d'une mélasse à l'autre, surtout si les mélasses contiennent du sucre inverti. L'acide sulfureux, à l'encontre de l'acide chlorhydrique, n'a pas d'action sur le pouvoir rotatoire du sucre inverti).

6°—La méthode à l'acide sulfureux décrite par M. Ogilvie en 1911, ne ressemble pas à la méthode à l'acide sulfureux indiquée par M. Pellet en 1891 & 1897. Elle ne lui emprunte que l'emploi de l'acide sulfureux. Elle en diffère par le but, par les moyens d'action, les quantités d'acide sulfureux, la durée de chauffage, dans le bain à 70°, l'interprétation des formules habituelles.

Même avec les modifications apportées par M. Ogilvie en 1911 et qui comportent plus de SO_2, elle ne peut être recommandée pour les mélasses de betteraves.

7°—Le moyen indiqué par Clerget en 1852 pour annhiler l'influence des matières azotées actives sur le sucre Clerget (ajouter à la polarisation directe les 2–7 de la différence entre la polarisation à gauche du liquide inverti neutre et du liquide inverti acide ne peut être recommandé.

8°—On peut employer, pour determiner le Clerget des mélasses normales de betteraves, soit la méthode de double polarisation acide Andrlik (dans le voisinage de 20° de température) soit la méthode Ogilvie par l'invertase, soit la méthode de double polarisation neutre avec emploi de chlorure de sodium ou de potassium pour la polarisation directe (Saillard).

Ces observations ne s'appliquant pas forcément au cas ou la mélasse de betteraves contient de la raffinose en quantités marquées.

9°—La méthode française Clerget, comme d'ailleurs la méthode Clerget-Herzfeld qui sont employées pour l'analyse commerciale des mélasses, donnent un sucre Clerget toujours trop faible et qui est surtout trop faible avec les mélasses contenant beaucoup d'azote (comme c'est surtout le cas dans les années sèches).

PHENOL-FORMALDEHYDE CONDENSATION PRODUCTS

L. H. Baekeland
Yonkers, N. Y.

The resinous or amorphous products resulting from the action of phenolic bodies upon formaldehyde have lately attracted considerable attention on account of their rapidly increasing applications for industrial purposes.[1]

It is questionable whether this general designation of "condensation products of phenols and formaldehyde" should be maintained much longer. Indeed, it is well known that these products can be obtained without the use of so-called formaldehyde. In fact, the first condensation products thus described were produced without the use of formaldehyde,[2] and it is generally accepted that other methylen compounds, for instance, methylal, trioxymethylen, hexamethylentetramin, etc., can replace formaldehyde in this reaction. The fact that hexamethylentetramin can suitably replace formaldehyde in the formation of the infusible phenolic condensation products was published as far back as December 31, 1907, by Lebach.[3]

Lately, I have succeeded in producing fusible resinous condensation products identical with those described by Blumer, DeLaire, etc.[4] by introducing a mixture of salicylic acid and an inorganic acid in the cathode compartment of an electrolytic cell in which sodium chloride is electrolyzed, a mercury cathode being used. According to the well known reaction of Kolbe, the carboxyl group of salicylic acid is introduced by reacting with CO_2 on phenolate of sodium. So that we have here an example of the possibilitiy of introducing indirectly the methylene group as CO_2, then reducing the carboxyl group by means of nascent hydrogen. A similar observation has already been recorded by Velden,[1] who expected to get oxybenzyl-alcohol by reducing salicylic acid but obtained the corresponding saliretin-body resulting from the dehydration of phenol alcohol.

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[1] Baekeland: "The Synthesis, Constitution and Uses of Bakelite," Journal of Industrial and Engineering Chemistry, Vol. 1, No. 3, 1909, page 149. "On Soluble, Fusible, Resinous Condensation Products of Phenols and Formaldehyde," Journal of Industrial and Engineering Chemistry, Vol. 1, No. 8, 1909, page 545. "Recent Developments in Bakelite," Journal of Industrial and Engineering Chemistry, Vol. 3, No. 12, 1911, page 932.

[2] Berichte 5 page 1905; 19 page 3004 and 2009; 25 page 3477; 27 page 2411.

[3] Knoll patent, Belgium, No. 204, 811, December 31, 1907. Ditto. Wetter (Knoll) British patent No. 28009-1907, owned by the Bakelite Gesellschaft of Berlin.

[4] Baekeland, "On Soluble, Fusible, Resinous Condensation Products of Phenols and Formaldehyde."

However, the designation "phenol-formaldehyde condensation products" has been so generally used, that for awhile at least, we shall have to submit to it as a matter of routine.

In the same, way, we are erroneously designating as "formaldehyde" a commercial aqueous solution containing some real formaldehyde or methylenoxide, CH_2O, with much methylenglycol, methylal, trioxymethlyene, hydrates of trioxymethylene, other polyoxymethylens, etc., all compounds of methylen of which the technical value is equivalent in this reaction to that of true formaldehyde.[2]

The direct relationship of the resinous condensation products to phenol-alcohols or their anhydrides, seems now pretty well established: The so-called fusible soluble resinous condensation products are merely varieties of the saliretins,[3] and all these products differ only from each other by greater or lesser fusibility, solubility, or hardness, and each of these properties can be modified at will. Furthermore, we have the means at hand of producing all these bodies diectly from phenol-alcohols.[1]

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[1] Velden Journ. Prak. Chemie. (2) 15 page 164. Jahresbericht 1877, page 337.

[2] Raikov. Chem. Ztg., 26, 135; 12; 11 (1901). Kekule, Ber., 25, 2435. Harries, Ber., 34, 635. Compt. rend., 124, 1454; Bull. soc. chim. 17, 849. F. Auerbach, also Auerbach and Barschall, Arb. kais. Gesundh., Band XXII, Heft 3 and Band XXVII, Heft 1, Verlag Julius Springer, Berlin.

[3] Beilstein, Organ. Chemie, Vol. 2, 1896, page 1109. R. Piria, Ann. Chem., 48, 75; 56, 37; 81, 245; 96, 357. Moitessier, Jahresbericht, 1886, page 676. K. Kraut, Ann. Chem., 156, 123; Gerhardt, Ann. Chim. Phys. (3) 7, page 215. F. Beilstein and F. Seelheim. Ann. Chem. 117, page 83, C. Schotten, Berichte, 1878, page 784.

The formation of ortho- and para-oxybenzyl-alcohol, or their homologs, by Manasse and Lederer, is sufficiently well known[2]; this process consists in the direct action of one molecule of phenol on one molecule of formaldehyde in presence of one molecule of NaOH under special conditions.

Then DeLaire[3] showed that these same phenol-alcohols can be transformed industrially by dehydration into fusible resins or saliretin products suitable for commercial purposes in place of shellac, copal, or other natural resins. In that process, it is not necessary to first produce the phenol-alcohol in pure form, and the two reactions can be carried out practically at the same time, so that the phenol-alcohol is dehydrated to saliretin resins as soon as it forms.

This is accomplished more directly by reacting with phenol on formaldehyde in presence of an acid,[4] provided the reaction be carried out under suitable conditions. One of the required conditions is that the phenol should be in excess so as to avoid the formation of variable amounts of infusible and insoluble products. A fusible soluble saliretin can thus easily be prepared which has all the appearance of a resin: it melts if heated and solidifies by cooling; it is soluble in alcohol and acetone; it can be maintained in fusible condition for very long periods, without becoming infusible or insoluble, provided heating be carried on below certain temperatures, and provided the excess of phenol be not removed. This fusible resin and its preparation has been described by Blumer, and DeLaire as a "shellac substitute," or "resin substitute[5]"; by Baekeland, who calles it "Novolak,[6]" and lately again by Aylsworth, who calls it "phenol resin.[1]" In whatever way it be obtained, whether by using a phenol-alcohol (DeLaire, Baekeland); whether by starting from phenol and formaldehyde in the presence of oxyacids (Blumer) or in the presence of mineral acids (DeLaire, Thurlow, Bayer), or by the action of phenol on formaldehyde without adding condensing agents, (Story[2]) (or Aylsworth) loc. cit.) the product is absolutely the same in its chemical and physical properties. Its melting point or fusibility may be modified at will by varying the amount of free phenolic body. This free phenol exists in solid solution in the mass and can be eliminated by merely physical methods; by the partial elimination of this free phenol, the fusibility and the solubility of the resin are decreased. The last traces of free phenol cling tenaciously to these saliretin resins; so much, indeed, that at one time, I was inclined to believe that this small amount of phenol was chemically combined. Indeed, the last traces of phenol cannot be expelled by heating at the lower melting temperatures of the product. There is nothing strange in this, if we take into consideration that phenol itself has a relatively high boiling point, and we know of numerous examples where colloids retain, physically, small amounts of other bodies which form therewith colloidal solid solutions. As long as there is some excess of phenol present in the saliretin, it is possible to maintain the mass in fusion for a practically indefinite time, provided the temperature be not raised too high. Pure saliretin, containing no excess of phenol, may be kept in fusion for some time, but after awhile it polymerizes and becomes less fusible until finally it changes into some infusible product. However, it should be noted right here that this latter product, although it is infusible, does not possess the maximum mechanical strength nor hardness, nor general chemical and physical resistivity, of those other polymerized infusible products, of which I will speak later on, and which are obtained by reacting with a sufficiently larger amount of formaldehyde, or equivalent methylene compounds, and which have been designated as Bakelite C.

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[1] Baekeland, "On Soluble, Fusible Resinous Condensation Products of Phenols and Formaldehyde," Journal Industrial and Engineering Chemistry, Vol. 1, No. 8, 1909, page 545.

[2] Journal Praktische Chemie (2), vol. 50, page 224. Ber. 1894, 2409/2411; D. R. P. Bayer, 85588; U. S. P. Manasse, 526786; 1894.

[3] DeLaire British Patent. 15517/1905; D. R. P. 189262.

[4] Blumer Brit. Pat. 6823/1903; 12880/1902; DeLaire French Patent 361, 539; Wetter (Knoll) Brit. Pat. 28009/1907; Knoll French Pat. 395, 657; Bayer, D. R. P. 237786; D. R. P. 201, 261; Brit. Pat. 26317/1907; etc.

[5] Loc. cit.

[6] Journal Industrial and Engineering Chemistry 1909, page 545.

It is possible to expel the slight excess of phenol which lends special fusibility to the so-called fusible resins; this can be accomplished whether these resins be called "shellac substitutes," "Novolak," or "phenol resins," or whether they be made directly from phenol alcohols, or from phenol and formaldehyde with or without acid condensing agents. Indeed, plain heating at 300° C. to 350° C. or better, heating in vacuo, or in a current of an inert gas, like nitrogen, easily expels the free phenol, and produces infusibility. The same result is readily obtained by entraining the free phenol by blowing superheated steam through the molten resinous mass.

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[1] U. S. Pat. 1029737.

[2] Austrian Pat. 30844, page 2 lines 17 to 20.

These facts are corroborating proofs to others which establish clearly the saliretin-nature of these fusible products, and demonstrate their relationship to the phenol-alcohols from which they are derived. If these fusible resins are prepared directly from phenol and formaldehyde, the preliminary formation of phenol-alcohol may escape our notice, because by the action of heat on the mixture especially in presence of acid bodies, the penol-alcohols are rapidly dehydrated to saliretin products. But it is quite possible to demonstrate their presence, and my assistant, Dr. A. H. Gotthelf, while preparing fusible resinous condensation products, by boiling a mixture of phenol and formaldehyde, acidulated by means of HCl, has been able to extract from this mixture, well defined crystals of oxybenzyl-alcohol before the heat had accomplished its resinifying action.

It is self-evident that as soon as high temperatures are applied to such mixtures, the formed phenol-alcohol will quickly undergo resinification, because the phenol-alcohol will be dehydrated to a saliretin product as soon as it is formed.

If there is an excess of phenol present, or if the formaldehyde reacts in insufficient proportions, which amounts to the same thing, a fusible saliretin will be the result.

In the absence of an excess of phenol, but using, however, a restricted amount of formaldehyde or other methylen compound, a polymerized infusible saliretin will be produced.

But whenever we succeed *in bringing into reaction a sufficient amount of formaldehyde* or its equivalent, then a much harder, much stronger and more resistive infusible body than an infusible saliretin, will be formed, and this body of maximum strength and resistivity is identical with Bakelite C.

If we first produce the pure crystalline phenol-alcohol, containing no excess of phenol, for instance crystalline saligenin or oxybenzyl-alcohol, and if we heat it gently, it will simply dehydrate and be transformed in a fusible mass which on cooling, solidifies to a resinous product—a fusible saliretin resin. The latter submitted to the further action of heat, polymerizes and becomes an infusible, insoluble saliretin. This polymerization is facilitated, by the presence of small amounts of catalyzers, for instance, hydrochloric acid. The presence of an excess of phenol retards polymerization; hence the infusibility induced by polymerization will be retarded, and this so long until some way or another the excess of phenol has been expelled. The infusible polymerized saliretin obtained by heating phenol-alcohols containing no free phenol, or by heating fusible saliretin containing no free phenol, is insoluble in alcohol, but swells in acetone; it soften decidedly on heating, although it is no longer fusible. Longer heating does not harden it further, nor make it more resistive. It is harder, stronger, and more resistant to physical and chemical agents than the fusible saliretin from which it is derived; in this respect, it surpasses even more the soluble fusible resins described by Blumer,[1] DeLaire,[2] Baekeland[3] and called "phenol resin" by Aylsworth.[4] But even after polymerization or hardening has been carried as far as possible, it is considerably less hard and less strong and less resistant to physical and chemical agents, than the polymerization products resulting from the reaction of phenol on a sufficiently larger proportion of formaldehyde or equivalent substances.

In order to obtain the latter polymerization products of maximum strength, hardness, and maximum resistivity, an adequately larger amount of methylen group must be introduced before or during the act of polymerization. The introduction of this methylen group may be accomplished by at least three distinct methods:

First method: Reacting directing with a sufficient amount of formaldehyde, or its equivalents upon phenol.

Second method: Reacting with formaldehyde or its equivalents on phenol-alcohol.

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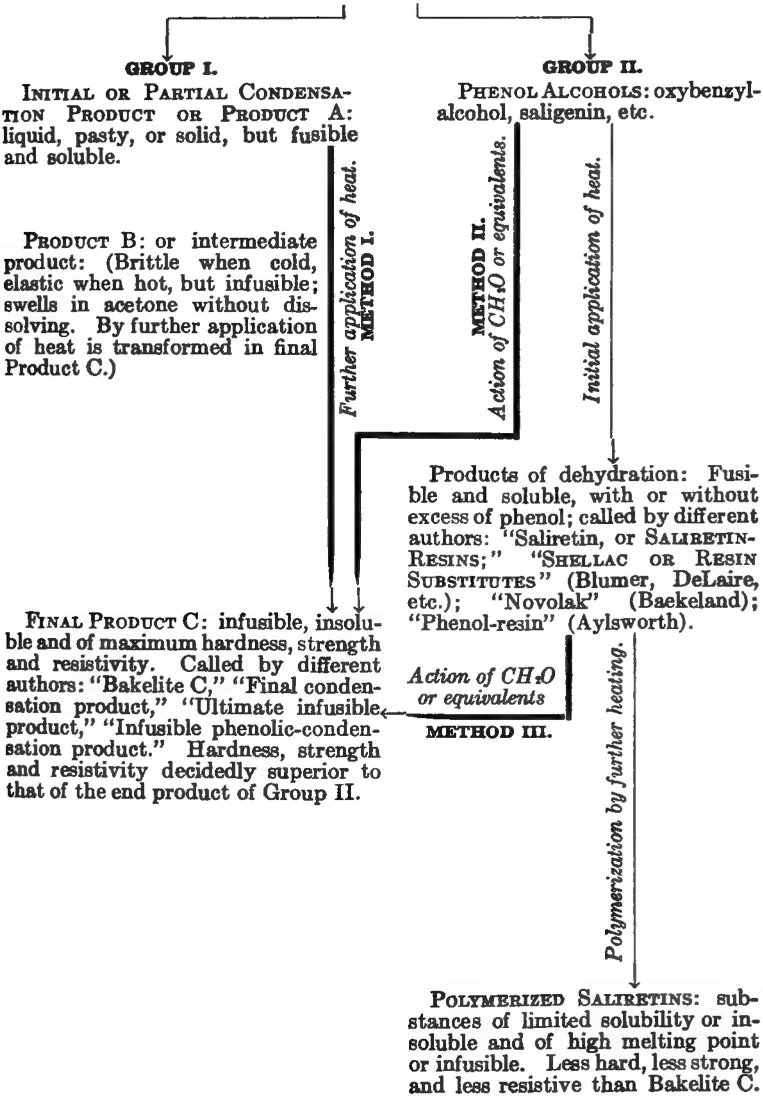
[1] [2] [3] [4] Loc. cit.

Third method: Producing a fusible dehydration product of phenol-alcohols or saliretin products, then reacting thereon with formaldehyde or its equivalents.

The following diagram describes very well all these relations.

PHENOL + FORMALDEHYDE (OR EQUIVALENTS) UNDER VARYING REACTING CONDITIONS FORM DIFFERENT BODIES


Further application of heat.
METHOD I.
METHOD II.
Action of CH_2O or equivalents.
Initial application of heat.
Action of CH_2O or equivalents
METHOD III.
Polymerization by further heating.

GROUP I.

INITIAL OR PARTIAL CONDENSATION PRODUCT OR PRODUCT A: liquid, pasty, or solid, but fusible and soluble.

GROUP II.

PHENOL ALCOHOLS: oxybenzyl-alcohol, saligenin, etc.

PRODUCT B: or intermediate product: (Brittle when cold, elastic when hot, but infusible; swells in acetone without dissolving. By further application of heat is transformed in final Product C.)

Products of dehydration: Fusible and soluble, with or without excess of phenol; called by different authors: "Saliretin, or SALIRETIN-RESINS;" "SHELLAC OR RESIN SUBSTITUTES" (Blumer, DeLaire, etc.); "Novolak" (Baekeland); "Phenol-resin" (Aylsworth).

FINAL PRODUCT C: infusible, insoluble and of maximum hardness, strength and resistivity. Called by different authors: "Bakelite C," "Final condensation product," "Ultimate infusible product," "Infusible phenolic-condensation product." Hardness, strength and resistivity decidedly superior to that of the end product of Group II.

POLYMERIZED SALIRETINS: substances of limited solubility or insoluble and of high melting point or infusible. Less hard, less strong, and less resistive than Bakelite C.

FIRST METHOD OR DIRECT METHOD. DIRECT ACTION OF PHENOL ON FORMALDEHYDE

Phenol can be made to react on formaldehyde or its equivalents at sufficiently high temperature so as to produce directly an infusible insoluble polymerization product of maximum strength and hardness (Bakelite C). In this reaction, the main requirement is that a sufficient amount of formaldehyde or its equivalents should enter into reaction. For this purpose, it is not necessary nor sufficient that the required amount of formaldehyde be merely present, because some of the formaldehyde may not enter into reaction or be lost during the operation. *The principal requirement is that the formaldehyde should react in sufficient amount on at least a portion of the phenol present*, even if some of the latter remains uncombined in the mass.

By the use of suitable methods, this reaction can be interrupted at its initial stages, so as to produce initial or partial condensation products which are temporarily fusible and soluble before further application of heat has changed them. These initial condensation products may be liquid, or pasty, or under specially favorable conditions, for instance by the use of small amounts of some bases, they may be prepared in solid form. At any rate, they are soluble in alcohol and acetone, and the solid variety is fusible. These fusible soluble initial products should not be confounded with the further advanced and intermediate product B, as described in my paper on "The Synthesis, Constitution and Uses of Bakelite." because the latter is insoluble and infusible, although it has not acquired the maximum hardness and resistivity which further application of heat will bring forth by changing it to condition C.

Further action of heat upon these fusible and soluble initial condensation products will ultimately cause polymerization and produce the final infusible and insoluble product of maximum hardness, maximum strength, and maximum chemical resistivity (Bakelite C).

By heating mixtures of phenol and formaldehyde in suitable proportions, at sufficiently high temperatures, for a sufficiently long time, chemical condensation may take place without the

Journal Industrial and Engineering Chemistry, Vol. 1, No. 3, 1909 page 149.

addition of condensating agents or catalytic agents; however, under such unfavorable condition, the action is too slow and too difficult to control for technical purposes.

By the addition of acids or acid salts, the reaction may be hastened to the point of becoming violent. But the presence of acid bodies tends to develop disturbing side-products which lessen the technical value of the final product. Furthermore, in presence of an acid reacting mixture, whenever there is a sufficient excess of phenol, we do not obtain the infusible, final product, but resins of the fusible saliretin—or "shellac substitute"—type. Things go quite differently if small amounts of bases are present during the reaction.[1] Small quantities of bases prevent radically the formation of fusible soluble saliretin products (shellac substitutes, Novolak, phenol-resin, etc.) and insure the formation of infusible, insoluble, final products, even in presence of a decided excess of phenol. If the phenol be used in excess, it will be found in the final product as a solid solution. In fact, the excess of phenol may be exaggerated to the point that the final product becomes very flexible or assumes a gelatinous appearance, and swells considerably in certain solvents, like phenol, or alcohol, or acetone, without, however, entering into complete solution. In any case, this free-phenol-containing substance is infusible; in other terms, the application of heat can no longer liquify it, although higher temperatures may char or destroy it.

This behavior of the bases constitutes a radical difference with that of acids or other acid-reacting bodies. Whenever acid-reacting bodies are used in conjunction with an excess of phenol, or an insufficient amount of reacting formaldehyde, (which amounts to the same thing), they tend to produce fusible soluble resins, while under exactly the same conditions and with the same proportions of phenol and formaldehyde, small amounts of bases develop surely infusible polymerized bodies as ultimate products.

In this method, the bases should be used in relatively moderate amounts; not in molecular proportions, as Manasse and Lederer[2] utilize them for making phenol-alcohols, nor as DeLaire[3] employs them to produce the fusible resinous dehydration products of these phenol-alcohols. Neither should they be used in such large quantities nor under such conditions as Hentschke[1] recommended for the manufacture of certain antiseptic compounds.

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[1] See Baekeland U. S. P. 942, 809.

[2] Loc. cit.

[3] Loc. cit.

If the amount of base be properly restricted, the reaction proceeds very regularly and remains under easy control. The base acts as an excellent accelerator, both in the condensation and in the polymerization. The use of bases under above mentioned conditions enables one to carry out the reaction with utmost uniformity and certainty of results.

At first sight, the importance of these seemingly modest facts, is not very apparent; no more than the value of the observation that sufficient counterpressure permits quick polymerization at high temperatures without risk of porosity; no more indeed than the realization of the fact that the final product with its great hardness, its strength and other splendid qualities, is unelastic and is woefully deficient for most industrial purposes where great resistance to shock or vibration is required, and that the incorporation of suitable fibrous materials improves all this by modifying the shattering wave induced by impact. Yet these are the three main factors which have enabled us to harness into technical service, an elusive laboratory reaction, and have rendered possible the creation of a new industry which is gaining daily in importance.

It has been shown[2] that small amounts of ammonia or amines may be used to good advantage for this purpose. It is a well known fact[3] that ammonia or ammonium salts, in presence of formaldehyde produce instantly a corresponding amount of hexamethylentetramin. In the same way, if any ammonia be added to a mixture of phenol and formaldehyde, a corresponding amount of hexamethylentetramin is produced, which can easily be extracted from the mixture. This fact was confirmed by Lebach, and can easily be ascertained by direct experiment.[4] It is self-evident that instead of a mixture of phenol and formaldehyde and ammonia, an equivalent amount of hexamethylentetramin or hexamethylentetramin-triphenol[1] may be used.

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[1] Hentschke D. R. P. 157,553.

[2] Baekeland U. S. Pat. 942,809.

[3] Wohl, Ber. 19, 1892; Tollens, Ber., 17, 653; Carl Goldschmidt, page 29. Bonn. Verlag von Friedrich Cohn. 1903; Cambier, Brochet, Compt. rend., 120, page 557.

[4] Lebach, Zeitschrift angewandte chemie. 1909, page 1600.

So that in the preparation of these bodies, formaldehyde can be replaced by hexamethylentetramin; this was already published by Lebach in the patent literature as far back as the end of 1907.[2] Whether the phenol mixture be prepared with ammonia or with hexamethylentetramin, its properties are practically the same, and on heating, both mixtures engender the same product, with final evolution of ammonia gas.

Whatever be the methods employed, this reaction is strongly exothermic, and heat is set free in the two phases of the reaction; first in the condensation stage, by which the initial condensation product is formed, and water is separated; then again in the final hardening when the product becomes infusible by polymerization, a considerable disengagement of heat takes place anew. If the substance be heated in thin layers, this self-heating may be unobservable on account of the heat losses, under such conditions; if, however, the mass is thicker or bulkier, and more specially if it be contained in a mold, this self-heating becomes very disturbing, and liberates gaseous or volatile products which cannot escape before the mass sets to infusibility; this causes the mass to swell and raise and to become porous, and makes it practically worthless for almost all technical purposes. This was the stumbling block which former investigators tried to avoid by conducting the hardening at very low temperatures, or by the use of suitable solvents which tend to moderate the reaction. This tendency towards foaming exists also if acid condensing agents are used, or even if no catalytic agents are added at all. The liberated gaseous products may vary according to conditions; in some cases, they may consist largely of formaldehyde gas, which tends to escape before the reaction is accomplished; if ammonia be used, and more so if hexamethylentetramin be employed, varying amounts of ammonia gas will be set free.

[1] The addition product of phenol and hexamethylentetramin. See Beilstein, Handbuch der Organischen Chemie, Third Edition Vol. II, page 651.

[2] Knoll Belgian patent, loc. cit., and Wetter (Knoll) British patent, loc. cit.

Specially when hexamethylentetramin is used, the evolution of ammonia is very abundant, and this naturally increases the tendency to foam and to give a porous final product. This tendency to foam becomes pronounced only at temperatures above 100° C., because at these increasing temperatures the exothermic reaction sets in. It should be noted that temperatures considerably higher than 100° C. are those which are employed in almost all commercial applications of these products, because they allow quick hardening and quick molding. At such high temperatures, polymerization proceeds very rapidly, but the exothermic reaction superinduces a further spontaneous increase of the temperature of the mass, and in this way, the defect of foaming is considerably more pronounced.

This tendency to foam, makes it of the utmost technical importance, whenever high temperatures are employed, for quick commercial work, that the liberation of gaseous or volatile products during the polymerization or hardening process, should be opposed by a suitable counter-pressure. The latter may be applied in various ways; for instance, by heating in closed molds, or in closed vessels, so that the imprisoned gases develop a suitable counterpressure; or by heating in a chamber in which air or other gases have first been pumped to a suitable pressure; or by heating in a hydraulic press. In the latter case, the first function of the pressure is to counteract the development of gaseous products, while at the same time, the mass is given the desired shape in the mold.[1]

For other applications, like varnishes or lacquer, where the material is applied in thin layers, the use of counterpressure is not indispensable.

As stated above, the use of ammonia or hexamethylentetramin increases the tendency to foam. On the other hand, small amounts of fixed alkalies, like caustic soda, act as more powerful accelerators than ammonia or hexamethylentetramin, without causing the evolution of disturbing ammonia gas or other gases. In this, and other respects, the fixed alkalies have decided advantages over ammonia or hexamethylentetramin, as well as over acid-condensing agents. For instance, they permit rapid hardening at the relatively low temperatures of 70° to 95° C.; furthermore, as soon as beginning solidification has set in, the temperature can be raised quickly to 110°, 120°, 160° C. At these higher temperatures, the hardening proceeds with great intensity and without fear that the gas bubbles should cause porosity. If the heating be carried to the hardening temperature, before all the water has been first expelled, then the only necessary precaution will be to keep the temperature sufficiently below 100° C. so that no steam should be evolved, which might cause blisters; but as soon as the mass has been heated long enough at these lower temperatures, so that it has solidified sufficiently, the temperature can be raised with impunity above the boiling point of water. As soon as these higher temperatures become available, the polymerization to final hardening advances very rapidly.

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[1] Baekeland, U. S. Patent 942,699.

For many purposes, it is simpler to drive off the water at temperatures below the polymerization temperature, either by drying in vacuo, or by drying in a stove at ordinary pressure at moderate temperatures, for instance 50° C. or below. Such dried material can now be submitted directly to relatively high temperatures without risk of blistering or foaming. This gives us the very best means for rapid hardening, as required by commercial processes. The use of these fixed alkalies has enabled us to carry on hardening and molding at a faster rate than is possible with ammonia or hexamethylentetramin, or other means, and at the same time to produce molded articles of better heat resisting qualities, of highest resistivity to solvents, chemicals, and of excellent dielectric properties. For many electrical purposes, the fact that no free ammonia exists in the mass, is a further advantage; indeed, this free ammonia is slowly liberated by heat from molded articles and sometimes may play rather disturbing pranks. It has a tendency to corrode brass articles.

SECOND METHOD

Action of formaldehyde or its equivalents on phenol alcohols: I have described this process in 1908.[1]

It has been shown that the best results are obtained if the amount of formaldehyde is at least one-sixth of a molecule as calculated to one molecule of phenol-alcohol. This same ratio holds good if substances equivalent to formaldehyde or to phenol-alcohols are used.

This method has enabled us to gain clearer insight in the relations of all infusible condensation products to the phenol-alcohols, and has furnished us the theoretical means for determining the optimum quantitites of reacting materials in our technical methods of manufacturing.

However, this process is more of theoretical than of practical interest, in as far as the third method accomplishes substantially the same result by starting from the anhydrides of phenol-alcohols.

THIRD METHOD

Action of formaldehyde or its equivalents, (Paraform, hexamethylentetramin, etc.) on saliretin-resins: The method is another indirect method and consists in first preparing a saliretin-resin of the fusible soluble type, then reacting thereupon with formaldehyde or an equivalent of formaldehyde.[2] This method was first published by Lebach at the end of 1907.[3]

In these patents, it is clearly mentioned that paraform and hexamethylentetramin are equivalent to formaldehyde in the preparation of condensation products. Furthermore, it is described how the condensation products may be prepared in two successive steps by adding the formaldhyde or hexamethylentetramin, or other equivalents, in two successive quantities. Briefly stated, the process consists in first preparing a fusible saliretin-resin, then to this resin is mixed a second quantity of formaldehyde, paraform, or hexamethylentetramin; this mixture submitted to heat produces the infusible product "C". In reality, we prepare here, in two steps, a product which is practically similar to the solid initial condensation product described in the first or direct method. In that method, the initial condensation product is obtained more directly by the addition of a sufficient amount of formaldehyde to phenol, in presence of ammonia, or other bases, or by the equivalent use of hexamethylentetramin or paraform. In the first or direct method, the reaction between the phenol and the formaldehyde ensues under elimination of water due to so-called chemical condensation. In the present case, however, a portion of the formaldehyde is first made to react on an excess of phenol, bringing about a corresponding elimination of water by chemical condensation; but in as far as the amount of formaldehyde is insufficient, a fusible saliretin-resin is formed. In order to transform the latter into the product "C", it is necessary to supply an additional amount of formaldehyde or some paraform, or hexamethylentetramin, etc. Hence the necessity of adding a certain amount of those methylen compounds to the fusible saliretin-resin, before the mass is submitted to hardening or polymerization by heat. The chemical reaction of the methylen compound on the fusible saliretin-resin, is accomied by the further elimination of water, which can easily be demonstrated by direct experiments.

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[1] The Synthesis, Constitution, and Uses of Bakelite; loc. cit. See also Baekeland Belgian addition patent #213,576; Baekeland French addition patent #11628.

[2] Baekeland U. S. Patent No. 1. 038,475, granted after interference with Aylsworth.

[3] Knoll Belgian patent No. 204,811, Dec. 31, 1907, and Wetter (Knoll) British patent 28009/1907, all owned by the Bakelite Gesellschaft, of Berlin.

If hexamethylentetramin is used, an abundant liberation of ammonia takes place at the same time; but even with the use of the latter, a certain amount of water is liberated by the action of the hexamethylentetramin on the free phenol contained in the fusible soluble saliretin-resin.

Barring those minor differences in preparation and proportions, the final product "C" is practically the same as what is obtained by the first or direct method as described above.

If hexamethylentetramin be added to the fusible resin, and heat be applied, the violent exothermic reaction which ensues causes an abundant liberation of ammonia gas. The mass rises like bread, and a hard spongy product is the result. Aylsworth[1] utilizes this foaming to prepare this substance in powder form by first producing porous masses of the final condensation product which can more easily be crushed to a fine powder than if solid lumps of this refractory material have to be pulverized.

In molding processes where high temperatures are needed, so as to insure quick hardening, this violent liberation of ammonia gas can easily be counteracted by suitable counter-pressure. In this case, the pressure is not only required for shaping the article, but first and foremost, for avoiding porosity. This can easily be demonstrated by heating the mass in an open mold, at the same high temperature as is used in the press; under these conditions, direct application of these high temperatures causes foaming and porosity, unless suitable counterpressure be applied.

It has been claimed that by the use of hexamethylentetramin in connection with perfectly dry fusible soluble phenol-resin, no water is liberated, which is supposed to be an advantage for certain applications where high dielectric properties are required. However, it should be noted that such fusible soluble phenol-resins all contain considerable amounts of free phenol and by the action of hexamethylentetramin on this phenol, water is formed besides the ammonia that is set free.

Moreover, the presence of large quantities of free ammonia is, if anything, more objectionable for certain purposes than the possible presence of small amounts of water.

It is true that free ammonia can be expelled by sufficiently long afterdrying of the molded articles, but by the same means it is just as easy to expel the last traces of water. This most striking fact is that there is no serious difficulty in obtaining articles of extremely high dielectric properties, even when starting from raw materials containing considerable amounts of water, provided the manufactured articles be submitted afterwards to a drying treatment which can be performed in any suitable drying stove.

It should be noted that almost all molded commercial articles made of phenol-formaldehyde condensation products contain various amounts of fibrous materials, preferably wood-pulp or finely divided sawdust. These organic fibrous materials, at the high temperature at which the molding in the hydraulic press takes place, (140° to 160° C, or over) begin to liberate variable amounts of water and other products of decomposition, which depress the dielectric properties. This is another reason why all molded articles intended for purposes where high dielectric properties are essential, should be submitted to oven-drying after they are molded. Those who are unfamiliar with the technical side of the subject may ask why it would not be simpler to omit altogether the use of fibrous organic materials. They might suggest the use of asbestos. But asbestos has other drawbacks, which limit its use. For instance, asbestos is a relatively poor insulator, and the strength imparted by its fibres is not so great as that imparted by vegetable fibre; furthermore, its specific gravity makes the articles compounded therewith very heavy; moreover, any asbestos compositions which have to be machined or milled, are very severe on the tools. Another objection is that asbestos compositions do not take the excellent and easy polish which can so easily be developed on articles made with wood-fibre compositions, nor do they possess the elasticity and strength of the latter.

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[1] Aylsworth Belgian patent 240,116.

It might also be suggested to drop entirely the use of any fibrous material, and to use amorphous or pulverulent fillers. But the technical requirements forbid this. Indeed, the main characteristic of the final phenol-formaldehyde condensation products, is that although they are exceedingly hard and resistant, and have a remarkably high crushing strength, their flexibility and elasticity are very limited. In regard to these latter qualities, they occupy a position between hard rubber and glass. A sudden shock or limited bending shatters them, and this would restrict enormously their technical applications. I found that the shattering wave induced by impact could be considerably modified by the suitable introduction of fibrous or cellular materials, like wood-fibre. This behavior is quite different from that of other plastics like celluloid, or rubber, which lose their best and characteristic qualities by the incorporation of filling materials. The phenol-condensation products, on the contrary, are enormously improved for commercial use, if compounded with filling materials, provided the latter be of a fibrous nature; in the latter case, they lose their natural brittleness, can stand shock and impact, without shattering; they can be rendered flexible and yet maintain all their other excellent properties of high resistivity to physical and chemical agents.

Hence, some of the most important industrial applications of these condensation products are precisely those where they are used in conjunction with fibrous bodies; for instance, they serve to impregnate fibrous materials like wood, pulpboard, and to indurate the latter, or to agglutinate firmly loose fibrous substances, like wood-fibre or fine sawdust, which then act as a structural skeleton distributed throughout the indurated mass.

This important technical result is easily demonstrated by comparing the enormous strength and resistance to impact or shock of molding compositions containing wood-fibre with others containing the same amount of structureless filling materials, for example, powdered materials. Compositions made with the latter will be found incomparably more brittle and very much less appropriate, if not entirely unsuitable for most industrial purposes, and more specially for molded articles where great strength is required.

Other important technical results are accomplished with the use of filling materials; for instance, the highest dielectric properties have been rendered possible by the joint favorable action of fibrous materials and heat and pressure.

It might be cited here that paper impregnated with these condensation products, and submitted to hardening under heat and pressure, has made it possible to manufacture sheets which show an astonishingly high disruptive test (puncture test), averaging 77,000 volts a. c. on sheets of $\frac{1}{16}$ of an inch thick, corresponding to 1230 volts per mil or about 48,500 volts per millimeter.

Under these favorable conditions, the vegetable fibre of the paper is thoroughly impregnated with the condensation product, and the high pressure has excluded the possibility of porosity induced by foaming.

THE NATURE OF THE RESINOUS CONSTITUENT AND ITS INFLUENCE ON THE QUALITY OF RUBBER

CLAYTON BEADLE AND HENRY P. STEVENS,
London Bridge, England

Caoutchouc always occurs in association with resinous matter in rubber yielding latices, in what form is at present unknown. The globules may consist of caoutchouc and resin in intimate association or some of the globules may consist of caoutchouc only and some of resin only. In the latter case a difference in the microscopic appearance might be expected, depending on a difference in the refractive indices. We have subjected latices to careful microscopic observation but have never noted any difference in the appearance of the globules from secondary tissue which could be attributed to difference in composition, but in the case of latex derived from the primary tissues (leaf petioles) of *Hevea* trees[1] the proportion of caoutchouc globules of normal appearance was small but the percentage of resinous matter, although higher than in normal latex, was not high enough to account for the small proportion of globules of normal appearance. The majority of the globules were about one third the size of typical caoutchouc globules with a lower refractive index. We recently instituted some further experiments on this point. It is well known that caoutchouc dissolves, but not very readily, in ordinary ether. Ether has a coagulating effect on latex, but by suitable dilution and adjustment of other details it is possible to extract latex with successive portions of ether in a separating funnel. If resin globules exist separately from caoutchouc globules, we should expect to extract practically all the resin with the first ether treatment, the resin being probably more soluble than the caoutchouc. We separated the latex into three fractions of 11 grams, 11.5 grams and 6.8 grams of dry solids respectively, which on extraction with acetone for 6 hours in a soxhlet yielded 2.56%, 2.44% and 2.16% respectively of resins. Had the latex contained isolated resin globules we should have expected a much greater difference between the resin contents of the three extracts. The result is interesting but not decisive. The proportions in which caoutchouc and resin are found in rubber vary within wide limits; as examples we have Jelutong or Dead Borneo, derived from the latex of a species of *Dyera.* The dry solids in this case contain roughly ten per cent. of caoutchouc, the remainder consisting mostly of resins (non-saponifyable). Good class rubbers such as those derived from *Ficus elastica* or *Castilloa elastica*[1] will contain from five per cent. in the former up to ten or fifteen per cent. in the latter, according to the age of the trees. Finally, well prepared *Hevea* rubbers contain only one to three and one-half per cent. of resinous matters, taking this as determined by acetone extraction. Higher figures than these are sometimes met with in the case of smoked sheets and are probably due to the absorption of some soluble constituant from the smoke. The average figure for sheet and crepe rubbers (1st latex) is about 2.5%. The relatively wide variations cannot be accounted for by the method of preparation, i. e. sheet or crepes. Lower figures are obtained by the separation of water soluble constituents from the acetone extract and subtracting the former from the latter. The proportion of acetone extracted matter soluble in water varies considerably. Also acetone does not extract the whole of the water soluble constituents as the figures obtained by direct water extraction of the rubber (1) may be higher than those obtained by water extraction of the acetone extracted matters (3). Also the acetone extracted rubber yields a further extract when treated with water.(4)

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[1] Beadle and Stevens, Journal of the Society of Public Analysts.

By direct extraction with water in a soxhlet pale crepes give usually .4% to .5% extract, pale sheets rather more and smoked sheets 1.0% to 1.5%.

The following figures for extracts may be quoted·

[1] Beadle and Stevens, Lectures on India Rubber, p. 232.

	(1) Water soluble	(2) Acetone soluble	(3) Acetone soluble extracted with water	(4) Acetone extracted rubber extracted with water
1. Pale crepe	.44	3.18	.60	.90
2. Smoked sheet	1.40	3.84	.56	——
3. Ditto another sample	1.24	3.64	.82	.44
4. Medium pale sheet	.68	3.92	1.50	——

All these figures are given as percentages reckoned as the original dry rubber. (3) represents the water soluble portion of (2).

Taking sample 1, it is curious to note that the sum of the water soluble material in the 3rd and 4th columns amounts to 1.5% while by direct water extraction, as in column 1, only .44% solids was obtained. A repetition of the experiment gave substantially the same results. Sample 3, columns 3 and 4, balance column 1 satisfactorily.

The residues left from acetone (resin) extraction experiments offered a suitable material for physical examination. The extracted rubber (plantation *Hevea* pale crepe) was mixed with sulphur in the ordinary fashion and vulcanized alongside of a portion of the same rubber which had not been extracted. There was a striking difference in the feel of the two vulcanized specimens, the acetone extracted specimen being soft and weak compared with the untreated rubber. It seemed as if the acetone treatment had in some way slowed the cure. The extracted specimen in some respects resembled a very much undercured compound. We therefore cured some of the compound at a higher temperature, but the product was not appreciably improved. We could hardly credit the removal of two to three per cent. of resin with such far-reaching effects on the quality of the rubber, and were inclined to attribute the deterioration rather to the treatment than the loss of resins. It was coceivable that *heating* in acetone vapour for several hours might have some depolymerising or other effect on the caoutchouc. We therefore proceeded to prepare further samples by extraction *in the cold.* In this series we included with the Para rubber a specimen of Rambong (*Ficus elastica*) rubber prepared by one of us in the East some time previously. The samples in crepe form were immersed in acetone in stoppered bottles put away in a dark cupboard. From time to time the acetone was poured off, distilled and put back again. The extraction was continued for 3½ months, at the end of which practically the whole of the resins were removed and the crepe, apparently unaltered in feel or appearance, was hung to air dry. The amounts of dry substance extracted in the two cases were—Para crepe 3.05% and Rambong crepe 7.04%. The rubbers were not mixed and vulcanized straight away but allowed to hang for three months to give them every opportunity for recovery, should the treatment have had any physical effect upon them.

The rubbers and duplicates, which had not been treated in any way, were then mixed with 5% of sulphur and all samples cured for 3 hours at 135°, 139° and 148.5°C.

The following table gives the results of physical tests on these samples for the cures nearest to those most suited to the individual rubbers. The samples were vulcanized in 1909, that is to say, are now about three years old.

HEVEA RUBBERS

Results of tests on one-week old specimens

Cure 3 hours at 139°C.

	Breaking strain grams per sq.mm.	Elongation original length = 1	Present condition
Untreated....	1974	10.5	Perished
Extracted	1553	8.5	Perished

Cure 3 hours at 135°C.

	Breaking strain grams per sq.mm.	Elongation original length = 1	Present condition
Untreated....	999	10.8	Good
Extracted	515	7.1	Partly perished

RAMBONG RUBBERS

Cure 3 hours at 148.5°C.

	Breaking strain grams per sq.mm.	Elongation original length = 1	Present condition
Untreated....	1163	13.7	Perished
Extracted	1115	8.7	Perished

Cure 3 hours at 139°C.

	Breaking strain grams per sq.mm.	Elongation original length = 1	Present condition
Untreated....	775	12.7	Good
Extracted	871	11.1	Perished

In regard to the *Hevea* specimens:—

It is apparent from the above tests that extraction under the most carefully regulated conditions lowers the quality. The specimens are weaker and less elastic after curing, but perhaps the most striking effect is deterioration on keeping. The cure at 139°C. is a little too high and both samples are overcured and have perished on keeping. The cure at 135°C. is not far from the best suited, the unextracted sample after three years is in fairly good condition but the extracted sample is extremely weak, although not wholly perished.

The same effects are seen with the Rambong specimens, although perhaps to a lesser degree. We tried a number of other cures which were found quite unsuitable and are not therefore given here in detail. The outstanding feature was the soft flabby lifeless feel of the resin extracted and vulcanized rubbers in contrast to the unextracted ones, although the raw rubbers appeared as if unaltered.

To ascertain if this effect were due to the nature of the solvent we made one further series of tests with Hevea crepe, using 90% alcohol in the place of acetone over a period of four months. 1.94% of resins were extracted, that is about two-thirds of the total extract obtained by repeated extraction with hot acetone. The mixing contained a proportion of zinc oxide.

The vulcanized specimens were 20 months old when tested.

That from the untreated rubber was in fair condition but that from the extracted rubber had a soft, flabby feel, although it could hardly be described as perished.

	Breaking strain gms. per sq.mm.	Elongation at rupture Original length = 1	% elongation at constant load (60 gms.)	Subpermanent set %
Untreated	1593	6.3	44.2	3.8
Extracted	419	5.8	76.2	12.6

The deterioration produced by extraction of resin or the greater part of it is very apparent. The effect produced is similar whether the solvent be alcohol or acetone and in the latter case whether employed hot or cold. It is not possible to say whether the deterioration is due to the loss of resin or to some physical effect of the solvent on the rubber. Further experiments are in progress for the solution of this problem.

THE PROLONGED ACTION OF MIXED ACID ON CELLULOSE

JASPER E. CRANE
Arlington, N. J.

In the course of some experiments made by the writer in 1907 an attempt was made to determine what products would be obtained if cellulose was exposed to the action of nitrating acid for a long time until the cellulose had completely dissolved in the acid. In the experiment described in the following, the course of this reaction was studied by analyzing the acid mixture and the cellulose nitrate at different times. No studies of this nature have yet been published, although several investigators have nitrated cellulose for long periods of time; as long as 16 days. The experiments by Hake & Bell,[1] Berl & Klaye [2] and G. Lunge,[3] were for studying the effect of time on the nitration of cellulose rather than the formation of by-products and decomposition products, as in this experiment. Hauesserman [4] has studied the product formed by dissolving cellulose in nitric acid and precipitating with water, but quite different products are obtained here.

In order to affect as little as possible the composition of the acid bath, a sample of cellulose was given a short nitration in mixed acid of the same composition as the acid bath used in the experiment. The product was washed and dried and was then completely soluble in methyl alcohol, ether-alcohol, etc., and contained 11.37% nitrogen. The acid bath had the following composition:

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[1] J. Soc. Ch. Ind. 1909: 457.
[2] Z. ges. Schiess u. Spreng 1907: 403–6.
[3] Z. f. ang. Ch. 1906: 2051–58.
[4] Z. ges. Schiess u. Spreng 1906: 39 and 1908: 303.

63.30% H_2SO_4
18.11% HNO_3
.10% N_2O_3
18.49% H_2O

10 grams of the anhydrous nitrated cellulose were immersed in 1000 grams of the mixed acid in a stoppered bottle, sealed, and allowed to stand at room temperature, 20 to 25° C., for a total time of nearly four months. At the end of this period the cellulose nitrate was entirely decomposed and dissolved and the acid bath had become a clear liquid. During this period the pyroxylin and acid were sampled from time to time by shaking the bottle thoroughly and quickly pouring a portion of its contents upon a platinum cone, held in a funnel which delivered the acid into a bottle.

By shaking the bottle before each sampling the same concentration, or proportion of pyroxylin to acid, was kept throughout the course of the experiment.

The pyroxylin remaining on the cone was washed in water until neutral, dried, desiccated and examined. The percentage of nitrogen was determiend in a Lunge nitrometer, a test made for fixation of basic color to indicate the degree of hydration (methylene blue being the color used), and the solubility in various solvents taken. The acid was analyzed in the usual manner for sulphuric and nitric acids. The low oxides of nitrogen were determined by a colorimetric method and oxalic acid was determined by precipitation as calcium oxalate. Checks on these two determinations were obtained by titrating against potassium permanganate solution, which determined the total oxidizable matter in the acid.

The table below gives the composition of the mixed acid at each sampling; the percentage of nitrogen in the pyroxylin and the milligrams of methylene blue fixed by 1 gram of the cellulose nitrate. The curves show the percentage decrease and increase of the various constituents during the course of the experiment.

	Mixed Acid					Pyroxylin	
Time	H_2SO_4	HNO_3	N_2O_3	$H_2C_2O_4$	H_2O	% Nitrogen	Mg. Methylene Blue per 1 g.
Days							
0	63.30	18.11	.10	—	18.49	11.37%	2.3 mg.
1	63.34	17.93	.18	—	18.55	11.99	
2	63.38	17.93	.18	—	18.51	12.15	1.4
7	63.25	17.81	.25	.10	18.59	12.19	1.5
14	63.26	17.74	.29	.12	18.59	12.13	0.7
42	63.27	17.46	.37	.17	18.73	11.99	3.2
71	63.30	17.17	.49	.31	18.73	11.92	6.9
117	63.37	15.45	1.19	.41	19.58	——	—

Examination of the data shows that the percentage H_2SO_4 in the acid remaind constant throughout, the percentage HNO_3 decreased steadily, 2.66% of nitric acid being reduced; the low oxides increased 1.09%, and the percent water increased 1.09%. The reaction expressed in its simplest form is as follows:

$$2\,HNO_3 - N_2O_3 + H_2O + {}_3O.$$

The oxygen reacting with the cellulose nitrate caused a gradual oxidation. From the equation above 2.66% H_2O_3 would produce 1.60% N_2O_3 as against the increase in N_2O_3 of 1.09%, indicating that some of the nitrogen oxides left the acid in the form of the less soluble NO; it being established by Robertson & Napper[1] that cellulose nitrate in decomposing evolves NO and NO_2. 2.66% HNO_3 would produce .38% of water as against 1.09, increase as found, the balance coming from the decomposition of the cellulose molecule. The reaction mixture contained 1% cellulose nitrate, or 0.285% carbon. This would yield 0.83% oxalic acid instead of 0.41% as found, showing that the oxidation was only half finished.

The percentage of nitrogen in the pyroxylin reached its maximum in 7 days and began to decrease at the 14th day. The physical appearance of the pyroxylin up to and including the 7th day was normal; at the 14th day the pyroxylin became tender and began to break up in small pieces; on the 71st day the decomposition had proceeded so far that the pyroxylin was in the form of small flakes until finally on the 117th day it was completely dissolved. The fixation of basic color coincides with the percentage of nitrogen and the physical appearance of the pyroxylin showed that the dehydrating action was continued up to the 14th day, after which time the molecule was broken down and became further hydrated.

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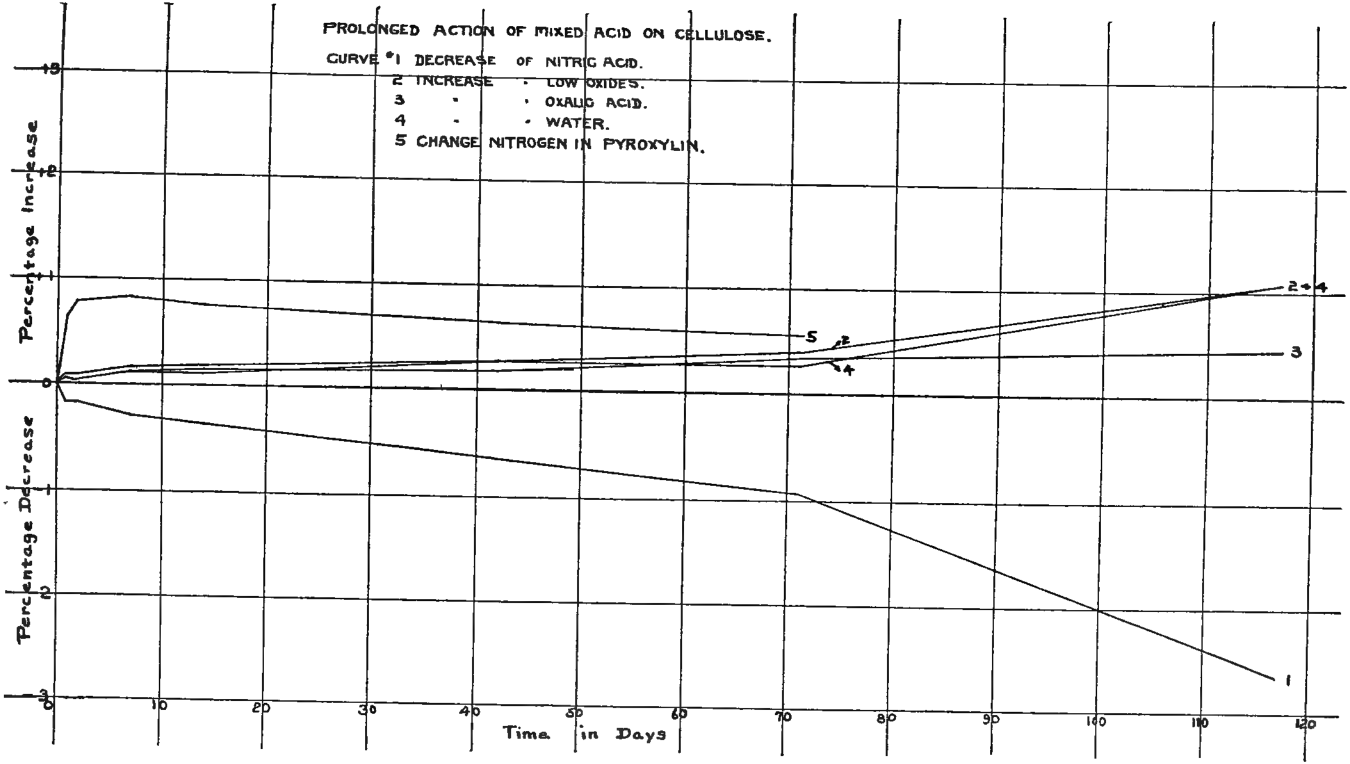
[1] J. Ch. Soc. 1907; 764–786.

The course of the reaction was a steady, but very gradual oxidation of the cellulose molecule, accompanied at first by a slight dehydration and later by considerable hydration; at first by nitrating action and later by a slight denitration. The intermediate substances formed are undoubtedly very complex, but the end product is oxalic acid. Remarkable stability, or resistance, to mixed acid is shown by the cellulose molecule.



PROLONGED ACTION OF MIXED ACID ON CELLULOSE.

CURVE #1 DECREASE OF NITRIC ACID.
2 INCREASE " LOW OXIDES.
3 " " OXALIC ACID.
4 " " WATER.
5 CHANGE NITROGEN IN PYROXYLIN.

SO-CALLED "OSAGE ORANGE RUBBER"—A PRODUCT OF KANSAS

CHARLES P. FOX
Akron, Ohio

Dispatches dated Lawrence, Kansas, November 10th, 1912, and, widely published by the press throughout the United States, announced the discovery by Professors Emerson and Roess of the chemical department of the University of Kansas, of rubber or a rubber-like substance in the fruit of the common osage orange.

The osage orange is a small native tree of the southwestern section west of the Mississippi River. Named from the Osage Indians, whose original home was on the banks of the Osage River in Western Missouri. This tree furnished these Indians with their bows and its fruit made their war paint. It was the Bois-d'-arc of the early French trader.

In its native habitat on the rich alluvial soil it reaches the height of sixty feet, and is a foot or more in diameter. In the north we know it only as a hedge plant.

It is easily recognized by its bent and erratic branches, tough fibrous bark, hard yellow wood, red roots, deep green, alternate, obovate entire leaves on long supple thorny branchlets, and large, greenish yellow fruit full of sticky milky juice. It is this intense stickiness that gives the idea of rubber.

Large trees furnish a hard durable timber used in wheels and posts. Its greatest use is as a hedge plant and for this purpose on account of its hardiness (will grow as far north as Albany, N. Y.), rapid and vigorous growth, ability to withstand the drought, indifference to the quality of the soil, its power to repel stock, its cheapness and ornamental appearance, it can not be surpassed. Its drawback is the long surface roots and its great drain upon the soil fertility. During the early seventies, considerable areas were planted out as source for silkworm forage. The fruit is worthless excepting for its seed for propagating. The possibility of a dual value of the fruit from rubber and seed, and the wide area over which it could be grown aroused considerable excitement among the rubber people of Akron. Theoretically, the fruit should yield rubber, the osage orange being one of the Artacarpaceae, a tropical order of 240 species distributed among 31 genera. The economic products given by this family embraces poisons, foods, fruits, rubber, timber and ornamental plants. Assam and "flake" rubbers belong here.

Four genera, Ficus, Morus, Broussonetia and Toxylon (Maclura) are represented in the United States.

Our tree is the *Toxylon pomiferum.* In many respects its fruit resembles that of the jack fruit tree of Borneo. The durian is the favorite fruit of the Malay. Durian rubber is of low grade, soft and resinous.

The great interest shown in the Kansas rubber led us to complete an investigation begun in 1904. The notes are:

"Ripe fallen fruit gathered in the latter part of Oct., immediately after frost. Fruit sound full of milky juice and retaining the characteristic odor of the fruit. Examination made while fruit was yet fresh. Selected apples were sliced, crushed in the washing rolls, the pulp and juice transferred to a flask, thoroughly extracted, first with acetone (to dehydrate), then with warm benzole and carbon-bisulfid, followed by hot water and finally with weak ammonia water. The organic solvent solutions were combined and evaporated. The hot water extracts were kept separate and evaporated. Evaporation and drying of these extracts were performed in a vacuum dryer.

1. Extract from acetone, benzole and carbon-bisulfid treatments amounted to 5.51%.
2. Extract from hot water treatment was 3.91%.
3. Extract from the ammonia water treatment was 6.76%.

Total extract was 16.18%.

1. The organic solvent extract was jet black, hard, brittle when cold, melting at 60 degrees to a black tar like mass, tasteless, slight odor of the original fruit and waxy feel, saponifies almost completely, the resulting alcaline solution giving up a bulky reddish brown precipitate on addition of a slight addition

of acid. This product melts in hot water to a reddish brown resinous mass.

The benzole treatment of the crude extract leaves a slight amount of a black friable powder soluble in water (water extract accidently present).

Addition of an excess of acetone to the benzole solution did not give a precipitate. (*Absence of rubber.*)

The acetone solution resulting from the above operation gives when evaporated, a jet black solid with many of the properties given above. Most important and peculiar characters are:

Insolubility in naphtha (characteristic of Spiller's resin); a benzole solution was precipitated by naphtha. Carbon-tetra chloride solution of the extract when treated with the bromine-iodine rubber reagent gave, on standing, a black, thick, soft product easily soluble in Weber's reagent (indicates a decomposition product of rubber). Sulphur Chloride precipitated from the benzole solution a yellow powder. Reaction immediate; very small quantity of the reagent required. Solution did not gelatinize (differs from rubber). The yellow powder was partially soluble in acetone, and wholly soluble in alcoholic potash, with strong disagreeable sulfur odor, characteristic of the sulfur chloride compounds of low grades resinous rubbers.

The extract did not give a definite reaction when fused with sulfur. All things considered the resin resembles a decomposition product of rubber, but lacks the characteristic odor of these compounds. The substance may be an immature stage of rubber: it is hardly a polymer.

It may be possible that the fruit of this tree, when grown in the hot dry climate of southern Kansas produces a true rubber. It would be interesting to compare fruits from the two sections. It may be interesting to note that the resin is soluble in benzole, carbon and acetylene-tetra chlorides, chloroform, carbon-bisulfid, nitro benzole, aniline, glacial acetic acid, methyl and anyl-acetates, xylol, alcohols, phenol, toluol and essential oils. Slowly soluble in ether.

Insoluble in naphtha, fixed oils and glycerine.

2. Hot-water Extract

Solid, shining, black, friable, bitter taste, chicory odor; does not melt, chars with a light flame and nitrogenous odor. Easily and completely soluble in cold water. Solution neutral or slightly alkaline. Alkalies do not precipitate. Alcaline earths give brown precipitates. Mineral acids give black precipitates. These precipitates melt and float in the boiling liquid: liquid portion turns red. *Organic acids* do not give this reaction.

Solution of salts like barium, lead and iron give similar brown precipitates. Formaldehyde and gelatine solution do not react. Fehling's solution is not reduced by the original solution; inverted solution gives a tannic acid odor but does not give a glucose reaction (not a glucoside), or the gelatine or iron tests for tannin. The general characters of this extract are similar to that obtained from the guayule plant.

The reddish black powder is insoluble in the usual rubber and resin solvents. Slightly soluble in hot glacial acetic acid, cold glycerine (slowly on standing). Partially soluble in cold concentrated sulfuric acid, boiling chars the substance and reduces the acid. Partially soluble to a wine-red solution in cold concentrated nitric acid. Insoluble in either cold or hot concentrated hydrochloric acid.

3. Ammonia Water Extract

Dull black, solid, harder and less soluble than the hot water extract. The crude material is evidently a mixture of two or more substances, probably an albuminoid, and pectic acid. The only constituent found being of any particular interest to the manufacturer of rubber goods, is the resin-like substance. This material on account of its great similarity to cheap resins, the small quantity present in the fruit, the low yield of fruit per tree (only stammate trees bear fruit), the length of time (10 years) to grow a tree to bearing age and the small scattered acreage now planted, is not likely to influence the rubber trade to any extent.

If any great benefit arises from the stimulated interest in the osage orange, it will be in the utilization of this tree in the production of a valuable timber upon waste land.

The most interesting point presented by the subject is whether the Kansas grown fruit of this tree is really any different from that of the Ohio grown fruit.

ON SOME PRELIMINARY OBSERVATIONS REGARDING THE CAUSES OF NATURAL CHANGE IN THE LATEX OF *HEVEA BRASILIENSIS;* AND ON THE DEPOLYMERISATION OF CAOUTCHOUC AND ITS CONVERSION

G. Stafford Whitby
Straits Agency

As a result of observations made in the East on the latex of cultivated *Hevea Brasiliensis*, the author has been led to the hypothesis that, in order adequately to explain the changes that spontaneously occur in such latex, it is necessary to assume the activity of four agencies, namely: a coagulating enzyme, an oxidase, anaerobic putrefaction, and aerobic putrefaction.

The Obvious Changes in Latex

Immediately latex issues from the tree, careful testing will show it to be faintly alkaline; but its reaction begins to change at once; and within a very short time (say half an hour) the latex is faintly acid. If some undiluted latex (not as a thin film, in which evaporation is a factor; and not in direct sunlight) is now allowed to stand in the air, the acidity will gradually increase; and the latex will, within a few hours—ten, at the most—have become a solid mass. Coagulation is not absolutely complete, since a little milky liquid can be squeezed from the mass. There is no smell—or, rather, merely the slight smell associated with fresh latex; the whole is perfectly white; and the liquid and coagulum are acid. If the latex is now allowed to stand further for twelve hours—i. e., over night—it will be found that the mass now smells decomposed; the surface is yellow or light yellow-brown, alkaline, and slimy; the liquid is still acid and so is the mass of the coagulum under the surface; and probably the under surface and lower parts of the sides of the coagulum are lacunose, owing to the development of bubbles of gas. If the mass is allowed to stand for a longer period, it is found merely that the above condition is accentuated; the alkaline slime becomes somewhat deeper, and the mass becomes more putrid, but no darkening of the coagulum occurs. Throughout, the serum remains milky.

The rate of change and its products are considerably altered if the latex is diluted. The amount of alteration depends chiefly upon the amount of dilution to which the latex is subjected; but, in general, the effect of dilution is: 1.) greatly to retard the formation of a coagulum; 2.) to retard the appearance of an alkaline reaction at the surface; 3.) to allow oxidative discolouration of the coagulum; 4.) to avoid the generation of gas bubbles and thus of lacunae in the slowly-forming coagulum. It would appear, in fact, that the series of changes leading to coagulation and putrefaction in a concentrated latex, takes place much more slowly if the latex is diluted; with the result that secondary reactions have time to occur.

A number of observations were made with the object of examining more closely the changes thus noted and of elucidating their causes.

THE OXIDASE: HEVEASE

As a result of an examination of an aqueous extract of Brazilian Para rubber, Spence[1] recognized the presence of an oxidising enzyme (or oxidising enzymes) which was, in the nomenclature introduced by Bach and Chodat, a "peroxydase." Spence failed to find any evidence of the presence of an "oxygenase." He recognised "oxygenase," however, in the latex of *Funtumia elistica:* and assumed that there must also occur an "oxygenase" in Para rubber.

A large number of samples of fresh latex from cultivated Hevea trees have been examined—from trees of all ages up to fifteen years; from original bark and from renewed bark; from trees marked out on various, tapping systems; half herring-bone, basal V, and upper Vs; from trees giving white scrap, and from trees giving black scrap; but in all cases it has been found that whilst a strong reaction for "peroxydase" has been obtained, universally negative results have been obtained for "oxygenase." The reagents used were chiefly tincture of guaicum and pyrogallol, the latter of which gives within ten minutes a yellow color.

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[1] Spence, D. On the presences of oxydases in india-rubber, with a theory in regard to their function in the latex. Biochem. Jour., Vol. III, 165.

The frequent failure to obtain the test for "oxygenase" in extracts of plants is explained by Bach and Chodat on the assumption that, owing to its great instability, it is destroyed during the preparation of the extract. Spence [1] suggests that its failure in the extract of Para rubber may be because the "oxygenase" is not got at directly on account of its association with a large mass of colloid material or because of its destruction during the coagulation of the latex.[2]

None of these explanations would seem to apply to the negative results for "oxygenase" here recorded. In addition to testing latices on their arrival at the laboratory—some three hours after tapping—latices have been tested in the field immediately they issued from the tree and within a few seconds of tapping; also with universally negative results. After several hours' standing with tincture of guaicum, no blueing occurred; but, if to the latex a little hydrogen peroxide was added, rapid blueing took place, and within two minutes the liquid was a brilliant blue. Tincture of guaicum was also put on the cuts so that it mixed with the latex immediately the latter had oozed forth; again with negative results.

The test was usually conducted thus:

1 c.c. latex mixed with
(5 c.c. water
((.5 c.c. hydrogen peroxide. 1 vol.))
and 1 c.c. tinct. of guaicum.

Further, several cases were selected in which if "oxygenase" occurred at all it should have been recognised. These cases were several ten-year-old trees which had been noticed for many months past as having been giving, from certain cuts, latex which very rapidly turned dark and produced black scrap on the trees and in which, presumably, oxidising enzymes were particularly active. The latex from these cuts was tested with tincture of guaicum immediately it issued from the tree; but in no case gave any blueing without the addition of hydrogen peroxide. The latex on the cuts had in these cases usually begun to darken naturally within fifteen minutes of tapping. It is interesting to notice that in the cases of the rapidly darkening latex just referred to the blueing with tincture of guaicum and hydrogen peroxide occurred more rapidly than in the case of normal latex; within ten seconds a dark blue had developed.

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[1] *Ibid.* With regard to the question, raised incidentally by Spence, in this paragraph, as to the temperature of the smoke when curing is carried out according to the Brazilian method, the present author would say, as a result of his own experiments on smoking, that it is about 65°.

[2] Moore, B. and Whitley, E. The properties and classification of the oxidising enzymes, etc. Biochem. Jour., Vol. IIII, 136, 1909. *Moore & Whitely's view is supported by the observations of Whewell, Proc. Roy. Soc., p. 124, July 20, 1911, on the direct application of tincture of guaicum to plant tissues.*

It would appear that the oxidase is much more active in these latices than in normal ones. In this connection reference may be made to a phenomenon which has been noticed repeatedly, and which indicates a tendency to more vigorous oxidase activity in the latex from the higher parts of the trunk than in that from the lower parts. In cases in which it is observed that a tree is giving from any or all the cuts at which it is being tapped latex which darkens exceptionally rapidly—passing through a pinkish stage, then through a purplish one to a grey one and, ultimately, becoming almost black—it is always found that the higher on the trunk a cut is situated the greater is the tendency to rapid darkening of the latex from that cut. It is frequently noticed, for example that, of the cuts forming a half herring-bone, the lowest one gives latex which does not discolour over a period of 24 hours; that from the middle cut becomes grey; and that from the top cut black. Even so small a distance as seven inches up the trunk may make a distinct difference in the tendency to darkening; the latex from the top of an oblique cut, the vertical distance between the top and the bottom of which is seven inches, becoming black, whilst that from the bottom of the cut has become light grey only. The significance of the greater oxidase activity as one ascends the trunk cannot yet be properly explained.

It should be pointed out that it is not permissible to employ large quantities of hydrogen peroxide, in conducting the test for oxidase in fresh latex since hydrogen peroxide alone, if present in sufficient quantity, coagulates latex. If so much hydrogen peroxide is employed that coagulation of the latex occurs, guaicum fails to respond to the presence of oxidase. This is due to the fact that hydrogen peroxide, when present in such amount, inhibits the action of the oxidase. Rubber from latex coagulated with hydrogen peroxide was perfectly white and undecomposed after 48 hours; and no discolouration or putrefaction occurred during drying. Small quantities of hydrogen peroxide, however, retard coagulation. In an experiment, 1 c.c. of 30-volume hydrogen peroxide prevented coagulation over night in 200 c.c. of a 10% latex.

It thus seems certain that the latex of *Hevea Brasiliensis* does not contain an "oxygenase." Bach and Chodat's conception of "oxygenases" and of the necessity for assuming the joint action of two enzymes—an "oxygenase" and a "peroxydase"—has been strongly criticised by Moore and Whitley,[1] who regard the so-called "oxygenases" as merely unstable organic peroxides. The oxidising enzyme found by Spence in Para rubber, and now recognised in the fresh latex, is sufficiently accurately described, without prejudice, as merely an oxidase, for which a suitable name is Hevease.

Spontaneous Coagulation in the Absence of Air

That natural coagulation is not dependent upon the activity of the oxidase can be shown in several ways, but the most striking proof is found in the fact that the spontaneous coagulation of latex occurs as easily in the absence of air as in its presence. If fresh undiluted latex is introduced into a bottle so as to fill it completely and the bottle is then stoppered and sealed, it will be found that coagulation occurs as rapidly and completely as in the same latex allowed to stand in the air. If the bottle is opened after some 7 or 8 hours, it is found to be filled with a mass of coagulum, there is no smell or discolouration and the coagulum and liquid are acid. If latex be allowed to stand in the absence of air for a longer period, the only further changes that are obvious are that the serum becomes perfectly clear, and that a certain amount of pressure develops in the vessel, due to the generation of gas. This gas contains carbon dioxide and hydrogen sulphide and often honeycombs the coagulum. No discoloration occurs, but a certain smell of putridity develops. A number of bulbs that were filled with latex ten months ago and hermetically sealed still show no further change; they contain a perfectly white coagulum floating in a clear and colourless serum, and also a certain amount of gas. Also, a number of bottles in which latex was sealed in the absence of air 12 months ago are now in a similar condition.

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[1] Moore, B. and Whitley, E. The properties and classifications of the oxidising enzymes, etc. Biochem. Jour., Vol. IIII, 136, 1909. *Moore and Whitly's view is supported by the observatiens of Whewell, Proc. Roy. Soc., 124, July 20, 1911, in the direct application of tincture of guaicum to plant tissues.*

The serum was further examined. The degree of acidity of the clear serum from a bulb, which had been sealed for 9 months was determined. 10 c.c. required 5.4 c.c. deci-normal sodium hydroxide. (The latex originally sealed up in this bulb was diluted latex containing ca 10% rubber.)

The serum always gave a slight but definite xanthoproteic reaction. Negative results were obtained with the Adamkiewicz reaction, with Morner's reaction for tyrosin, with the pinewood reaction for pyrrol, with the biuret test, and with Fehling's solution. Serum examined a few days after the latex had been sealed up gave a strong reaction for oxidase with tincture of guaicum and hydrogen peroxide (no reaction with tinct. of guaicum alone); but after it had been sealed up for nearly a year it did not react for oxidase. (The products and rate of aerobic change in this old serum were somewhat different from those in serum taken earlier).

It would appear that the result of anaerobic change in the latex of *Hevea Brasiliensis* is to produce first coagulation of the latex and subsequently anaerobic decomposition of protein (with its characteristic product, hydrogen sulphide) and possibly of other organic constituents of the latex. The cause of the first of these changes is probably a coagulating enzyme, which will be discussed later.

The subsequent aerobic changes that occur when such serum is exposed to the air have been examined and present in so far as they have been investigated, the general character of the aerobic fermentative change of protein break-down products. Usually the strongly acid and colourless serum gradually becomes dark brown and strongly alkaline. Very strong-smelling products (indole or skatole) may develop or they may not, depending, apparently, upon whether air has perfectly free access or not. If allowed to evaporate in the air, a sticky brown residue, very easily soluble in water to a dark-brown strongly alkaline solution, is formed.

The alkaline liquid produced by aerobic change of the serum effervesced vigorously with dilute mineral acid, evolving carbon dioxide. Its alkalinity was not due to ammonia, but probably to methyamine. On warming the solution with sodium hydroxide a gas, alkaline to litmus, was evolved. The solution gave a precipitate with platinic chloride (this ppt. was not merely the ppt. produced by acids and referred to later). The brown colour is probably due to humin-substances. Hydrochloric acid added to the solution produced a precipitate which was taken up again by alkalies. The humin-substances present are thus acid (melanoidinic acids, according to Schmiedeberg's view). This agrees with the conclusion of Samuely that the formation of humin-substances or melanoidins is dependent on oxidation and requires the access of oxygen.

The substances, the presence of which in the oxidised serum was demonstrated, bear a general resemblance to those which may be formed by oxidation from aromatic products of protein break-down. Tyrosin, when oxidized, is said to give homogentisinic acid, ammonia, and carbon dioxide.[4] Ellinger has shown that putrefactive bacteria may produce carbon dioxide by scission from the primary products of protein disintegration. Samuely views the humin-substances as, in general, being formed by a secondary reaction, from those primary products of protein disintegration which contain a benzene nucleus and nitrogen; and, although, in the serum under investigation, tests which indicate tyrosin, tryptophane, and pyrrol, gave negative results, there is reason to suppose—on account of the positive results obtained for the xanthoproteic reaction—that products containing such a nucleus are present.

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[4] Bertel, R. Ber. der deutsch. bot. Ges., 20, 460.

Probably both bacterial agencies and oxidizing enzymes play a part in the aerobic changes.

The Coagulating Enzyme

Further support of the idea that the activity of the oxidase in its relation to the production of discolouration in latex and coagulum is something quite distinct from the cause which results in spontaneous coagulation is found in the fact that the two phenomena—oxidation and coagulation—never run parallel; many reagents that prevent or retard coagulation accelerate oxidation. But perhaps the simplest proof is to be found in the fact that, when undiluted latex is exposed to air, the rapidity with which natural coagulation occurs is not dependent upon the surface which is exposed; coagulation takes place as quickly and completely in a tall narrow cylinder as in a flat open dish.

In considering the question as to the nature of the anaerobic agency which is responsible for natural coagulation, the first point to be considered is as to whether such coagulation is merely the result of the first stages of the activity of the same agency as that which results in the subsequent anaerobic putrefaction, which will occur if the latex is kept away from air, with its characteristic product hydrogen sulphide; or whether it is due to a different agency. It is reasonable to suppose that it is due to a different agency—of an enzymic character—as the following consideration shows. Latex was subjected to a sufficiently high temperature for a short time; and it was found that no coagulation occurred for several days; putrefaction then set in, and a coagulum formed. Now, under ordinary circumstances, concentrated latex begins to set to a solid mass in six hours. If coagulation were merely a phase of the initial activity of anaerobic putrefactive bacteria, the latex which has been heated should also coagulate a few hours after it has cooled, since infection with putrefactive bacteria must in any case occur after the latex has issued from the tree. Further, the rapidity with which coagulation occurs is not in agreement with the usual rate at which putrefactive changes occur; and, in addition, when the latex has first set to a solid mass, the smell is quite fresh.

Natural coagulation does not appear to be a result merely of the acid which develops in latex. In the first place it is sufficiently obvious that the coagulation which has been shown above to occur under anaerobic conditions is not connected with the hydrogen sulphide which is developed, because (1) the possible amount of hydrogen sulphide is too small to produce a sufficient concentration of hydrogen ions to coagulate latex or to account for the acidity of the liquid,[1] (2) hydrogen sulphide was shown experimentally to be incapable of coagulating latex, either when added in the form of a saturated solution, or when passed to saturation-point through latex; in fact, it acted as an anti-coagulant; the activity of the enzyme which brings about coagulation being inhibited by hydrogen sulphide, since the samples of latex so treated were uncoagulated after 48 hours. But it is more important to find that the process of natural coagulation does not appear to be dependent upon the gradual development of acid in latex which is allowed to stand, and is not brought about by such acid; since the development of acid takes place much more rapidly in diluted latex than in undiluted latex; and, at a time when little or no coagulation has occurred, the amount of acid in diluted latex may be much in excess of that which it would be necessary to add in order to bring about coagulation. In brief, the development of acid in latex and its natural coagulation do not occur *pari passu*. Thus, for example:

> At 11.30 a. m. two quantities of latex were put aside. (1) 50 c.c. undiluted latex; (2) 50 c.c. latex diluted with 250 c.c. water. 6½ hours later (1) was a solid mass (2) showed only a little floating coagulum. The acidity of (1) was equivalent to 4 c.c. deci-normal sodium hydroxide.

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[1] Beadle, Clayton and Stevens, H. P., Some analyses of Hevea latex. Analyst, Vol. XXXVI, 6, 1911, give 2.03 as the percentage of protein in the latex of a ten-year-old tree. Latex used in some of the experiments in this communication was from 15-year-old trees. Assume 3% of protein. Assume 1% sulphur in the protein; 1.088% being the highest result recorded by Osborne for the sulphur-content of a vegetable protein-excelsin. The sulphur in the ash of Plantation Para is inappreciable.

(2) was left over night, after which time not much coagulation had occurred; the acidity was then equivalent to 25 c.c. deci-normal sodium hydroxide.

It is known that in order to produce coagulation by acid the amount of acid which must be added is proportional to the total rubber-content of the latex and not to its dilution.

Latex was collected from the same trees as those from which the latex in the above experiment had been taken on the previous day. 50 c.c. were diluted with 250 c.c. water; and acetic acid equivalent to 25 c.c. deci-normal sodium hydroxide was added. As was expected, coagulation occurred rapidly; and, after 15 minutes, the coagulum had risen in the vessel, leaving a perfectly clearer serum.

The author regards the coagulation of Hevea latex as essentially a physical change, conditioned, in the case of natural coagulation, by preliminary chemical change brought about by enzymic action. The behaviour of latex to heat in relation to its dilution is illuminating. Samples of latex were heated immediately after their issue from the tree. Usually at about 67° the latex became a thick mass of agglutinated particles which did not cohere together. If the heating were prolonged, and the mass stirred, it became coherent at about 75°. Latex was allowed to stand for several hours (say for 5 hours), and then heated. The coagulation temperature (by which is meant the temperature at which a coherent mass forms) had fallen only a little; it was 71°. (The introduction of a little acid, by means of bubbling carbon dioxide through the latex, lowered the coagulation temperature to 63°.) In the case of diluted latex the change in the coagulation temperature on standing is much more marked, due, presumably, to the more rapid development of acid in such latex; it having already been shown that there is reason to believe that more acid develops naturally in dilute than in concentrated latex. Further, the coagulation temperature is greatly affected by dilution of the latex; the greater the volume of water in proportion to rubber the higher is it necessary to take the temperature in order to produce coagulation.

11 a. m. latex collected from the field and to which only a little water had been added was heated in a water-bath. At 85° the latex thickened, but the particles did not cohere. Just above 90° they cohered on stirring;

but coagulation was very incomplete, and, even after heating at 100° for some time, the liquid was still milky. Portions of the latex were diluted with water in the proportions 1:1, 1:4, 1:9. These diluted latices could be boiled without coagulation taking place. The original latex was now diluted with two volumes of water, and allowed to stand for 6 hours, at the end of which time its coagulation temperature was 66°. At this temperature curdling occurred sharply and a coherent mass formed at once on stirring. This latex (1:2) was now diluted with various quantities of water, with the following results:

Degree of dilution of original latex	Coagulation temperature
1:2	65°
1:5	72°
1:11	79°
1:23	84°

The effect of dilution shows that coagulation by a purely physical process—namely, heating—occurs less easily when the particles which form the colloidal emulsion constituting latex are distributed throughout a large volume of latex than when they are closer together. Now coagulation by added acid is, within ordinary limits, independent of the volume throughout which the rubber is distributed. Further, it has been shown (see *supra*) that natural coagulation takes place the less readily the greater the volume over which the rubber is distributed and is not, in relation to the acidity of the latex, independent of the dilution. Thus, natural coagulation appears finally as a physical process resembling rather coagulation by heat than coagulation by added acid. (Acids, it may be remarked, appear to be effective in producing coagulation in proportion to their hydrogen-content.)

The active agent in natural coagulation is, in all probability, an enzyme; since heating, which would destroy the enzyme, prevents coagulation (the subsequently coagulation, taking place after 2 or 3 days, is to be looked upon as due to putrefaction). Experiment showed that the enzyme was not of the nature of a lab-ferment. It is not improbably of a proteolytic character. Fickendey[1] suggests that coagulation of latex is due to the initial coagulation of the colloidal protein which has been exercising a protective influence. Assuming such protective action, possibly the coagulating enzyme under discussion may act in such a way as that conceived by Fickendey or by the partial disintegration of the protective protein; the great acidity which develops being due to other changes taking place, not in the protein, but in other (diffusible?) substances in the latex. As it stands, however, the matter requires further investigation.[1]

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[1] Fickendey, E., Koagulation des Kautschuks. Koll. Zeit., VIII, 43.

Since natural coagulation is due to an anaerobic change, it is probable that there is present in the walls of the lactiferous system an anti-ferment which prevents coagulation.

Conditions of Activity of Hevease

The oxidative activity, as indexed by the rate and amount of discolouration occurring in latex or in the coagulum, is often greatly increased by the addition of phenolic bodies. Phenol, pyrogallol, picric acid, and pyroligneous acid have such an effect.

> To 100c.c. of an ordinary diluted latex (ca 10%), 50c.c. of a 5% solution of pyrogallol were added. Within a few hours the surface had become brown and the mass of the liquid light brown. Five days later no coagulation or decomposition had occurred; but the latex was brown in color. It was now coagulated by a little mineral acid and washed, being converted into crêpe. When dry, the rubber was of a very dark brown color.
>
> To a further 100c.c. of the latex, 30c.c. of a .1% solution of picric acid (that is, insufficient to coagulate the latex) were added. On examination 18 hours later there was no sign of decomposition, but the surface was very discoloured.
>
> Again: quantities of 100c.c. were treated with 1.) 2c.c. semi-normal acetic acid, 2.) 2c.c. pyroligneous acid, 3.) .5c.c. pyroligneous acid. Within an hour 2.) was discoloured. Within 2 hours 3.) was discoloured. 1.) was perfectly white after 4 hours.

The greater amount of oxidation in the presence of phenolic bodies is of interest in reference to the mode of action of Hevease. It was found that the addition of small quantities of hydrogen peroxide not only retards natural coagulation, but that they have no effect in increasing the rate of oxidation. It would appear that the oxidative discolouration of latex and of the coagulum is due to changes produced in phenols or related bodies.

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[1] It may be recorded that Phosphotungstic acid added to latex produced rapid agglutination followed by coagulation. No further change was apparent after 24 hours' standing; the Phosphotungstic acid preventing discolouration and decomposition.

As regards the sensitiveness of Hevease to heat, it was found that latex which had been heated at 70° for ten minutes and then allowed to stand for three days (putrefaction had then occurred) still gave a marked reaction for oxidase when tested by hydrogen peroxide and tincture of guaicum. If heated to 90° for ten minutes, however, no reaction for oxidase was obtained. The oxidase in the extract examined by Spence[1] was destroyed by 15 minutes' exposure to a temperature of 70°.

A number of substances which greatly accelerate oxidase activity have been encountered. Silver nitrate added to latex either in sufficient quantity to produce coagulation or in small amount along with sufficient mineral acid to produce coagulation leads, within a minute, to a grey color, which extends throughout the mass of the coagulum. If the grey coagulum is kept away from the air no further discolouration occurs; but if it is exposed to the air, or if washed and converted into crêpe, extraordinarily rapid darkening occurs and within a few minutes the rubber is black on the surface. The crêpe was shown to contain silver. A similar rapid darkening was observed in the coagulum produced from latex which had been mixed with a colloidal solution of silver (containing NaOH). The coagulum in this case was brown, and whilst kept away from the air did not change. In the air, however, it rapidly became black.

Calcium chloride also exercises a marked influence on the activity of Hevease.

Working with an ordinary dilute latex (containing ca 12% rubber), it was found that the minimum amount of calcium chloride which would bring about coagulation was 5gms. per litre of latex. Using twice this amount, the oxidative activity was so greatly increased as compared with the rate in untreated latex or in latex treated with aliphatic or mineral acid that discolouration was apparent after only 20 minutes.

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[1] Spence, D. On the presences of oxydases in india-rubber, with a theory in regard to their function in the latex. Biochem. Jour., Vol. III, 165.

As the amount of calcium used increases, the rate of discolouration, whilst still large, decreases; and, as the amount of calcium chloride decreases, the rate of discolouration diminishes, and, in the case of .5gms. per litre, is, during 6 hours, nil; although this amount is capable of bringing about a considerable amount of coagulation. Using 5gms. per litre, it was found, on examination, that the liquid which could be squeezed from the upper part of the coagulum was light brown. A soluble brown product has been noted in other experiments (regarding the influence of acids on oxidation) as a result of the oxidation when such change is most marked. Such brown liquid is alkaline. The colourless liquid squeezed from the lower part of the coagulum is acid. The mass of the coagulum immersed in the liquid and thus protected from the air does not, of course, become oxidised. The serum from the latex coagulated with calcium chloride undergoes very rapid change when exposed to the atmosphere. A dark brown shiny film forms on the surface of the liquid and on the sides of the vessel; and the liquid becomes dark brown and alkaline. If stoppered up, away from the air, the serum remains unchanged.

That a certain amount of Hevease and of other substances can be retained very firmly (adsorbed?) by the coagulum can be shown in several ways. Reference has already been made to the retention of silver; and in the case of calcium chloride a certain amount must also be retained; for, after very thorough washing of a coagulum prepared by calcium chloride, it was still found that oxidative discolouration occurred more rapidly than in the corresponding coagulum prepared by mineral or aliphatic acids. Reference may be made here to some observations as to the adsorption of dye by the coagulum, which appear to indicate that it is the protein of the coagulum which is concerned in the adsorption of substances present in the latex.

500 c.c. of latex (ca 12% rubber) were treated with 10 c.c. of a concentrated solution of ëosin; so that the whole presented a deep pink colour. Coagulation was brought about by acetic acid in slight excess. It was during its formation that the coagulum fixed dye; no further colour seemed to be extracted from the liquid after coagulation was complete. The coagulum was machined 1 hour after the addition of acid. The percentage of ëosin left in the serum was determined colorimetrically; and it was found that the coagulum had extracted 85% of the dye. The washed rubber was of a deep pink color and, when soaked in cold water, for several days, gave up only a little dye. It is probable that it is the protein that adsorbs the dye; because, whilst a piece of dry rubber of normal composition easily adsorbs ëosin, if allowed to stand in a solution of the

dye, a piece of almost chemically pure caoutchouc or a piece of rubber free from protein [8] adsorbed, after 48 hours' immersion, practically no dye.

Influence of the Condition as Regards Acidity of the Medium

The relation of acidity to oxidase activity, as manifested by grey discolouration of the latex or of the coagulum, has been examined. As stated earlier, no discolouration occurs in the course of the natural coagulation of concentrated latex. If, however, the natural conditions as regards acidity are interfered with by the introduction of extraneous acid, the oxidative changes that lead to such discolouration may occur.

1.) 100c.c. undiluted latex alone.
2.) 100c.c. " " plus 2c.c. normal sulphuric acid.

12 hours later, 1.) had become putrid and was light yellow-brown on the surface; 2.) was only slightly "rancid" and was grey on the surface. The surface in 1.) was alkaline; in 2.) acid.

[8] The sample of protein-free rubber here referred to was prepared by a modification of the method which Weber, from experiments on *Castilloa* latex, suggested. Weber suggested coagulation by the action of formaldehyde and sodium sulphate. The author finds that, in the case of Hevea latex, coagulation cannot be achieved by such a procedure; agglutination only occurs. (It may be noted that the author's experience leads him to conclude that there is no fundamental difference between creaming, agglutination (or, as it would be better described, flocculence) and coagulation. In experimental work the same latex often passes through all these stages; creaming first, then becoming flocculent and, finally—the flocks gradually increasing in size—becoming a coherent mass. The presence of formaldehyde in latex always tends to prevent the formation of a real coagulum; the latex merely flocculates. And it is very doubtful whether coagulation experiments made on latex preserved with formaldehyde have any value.)

The modification of Weber's method used was to treat latex at about 70° with a hot neutral solution of sodium sulphate in the proportion of 1 pound per gallon of latex. Flocculence at once began, but the rubber had not cohered after 2½ hours. Next morning, however, it was removable from the serum as a coherent mass. The coagulum was washed and converted into crêpe. The analytical figures obtained were: Ash, 1.485%; resin, 2.95%; insoluble in benzene, 1.1%. The insoluble was shown to consist of sodium sulphate and not of protein by extracting with water and determining the sulphate as $BaSO_4$.

In general it may be said that small amounts of acid accelerate the activity of Hevease, and large amounts diminish or inhibit it.

The fact that Hevease is not thus active in concentrated latex, but is so in diluted latex is seen to be related to the acidity of the latex. (The serum formed by the natural coagulation of concentrated latex reacts for oxidase by hydrogen and tinct. of guaicum.) The coagulation of latex occurs, and the change from an acid reaction at the surface to an alkaline one begins, much more quickly in concentrated latex than in diluted latex; and the production of grey oxidation bodies, which is to be regarded as merely a secondary reaction, has not time to occur. Such grey products can appear only so long as the surface of the latex in contact with the air remains acid. Whether the substances from which they are formed, by the action of Hevease, undergo, in concentration latex, further change too rapidly to give time for the action of Hevease; or whether the alkalinity developed at the surface inhibits the activity of Hevease; or whether the character or concentration of certain of the products of natural change in undiluted latex affects the activity of Hevease is not clear. It is interesting to note, however, that the coagulum formed naturally in concentrated latex will develop discoloured products if it is washed.

As regards the changes that result in the production of gas bubbles from the coagulum; it appears that the more air gets to latex during its natural coagulation, the less is the likelihood of gas bubbles—first of carbon dioxide and later of hydrogen sulphide—appearing. Latex in a long narrow vessel tends to show such gas bubbles more rapidly than latex in a flat, open vessel; and diluted latex, since the coagulum in it forms more slowly, develops less than the corresponding concentrated latex.

As regards putrefaction; extraneous acid, added to latex, retards or, if present in sufficient amount, prevents putrefaction.

The above points may be illustrated by reference to the effect of various quantities of hydrochloric acid on latex.

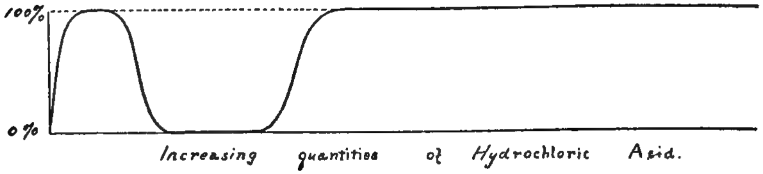
Quantities of 100c.c. each of a batch of latex as ordinarily handled, (i. e. containing ca 10% rubber) were mixed with gradually increasing quantities of HCl (1 in 10). 1.) .5c.c.; 2.) 1.0 c.c.; 3.) 1.5c.c.; 4.) 2.0c.c.;

5.) 2.5c.c.; 6.) 3.0c.c.; 7.) 3.5c.c.; 8.) 4.0c.c.; 9) 4.5c.c.; 10.) 5.0c.c.; 11.) 10c.c.; 12.) 15c.c.; 13.) 10c.c. of 1 in 5; 14.) 10c.c. of 1 in 2.5; 15.) 16c.c. of 1 in 2; 16.) 25c.c. conc. HCl; 17.) 100 c.c. conc. HCl; 18.) 200 c.c. conc. HCl. [In the last two cases the latex was added to the acid, and not vice versa.] After 5 hours: 1.) which was not coagulated), 2.), 3.), and 4.) were discoloured. They had become discoloured in the order named. 1.) had, in addition, begun to decompose slightly; it had the smell—best described as "rancid"—which is intermediate in such cases between freshness and putridity. 6.), 7.), .8), 9.), 10.), and 11.) were uncoagulated or coagulated only very incompletely. After 24 hours: 1.) and 2.) were putrid and yellow on the surface; 3.), 4.), and 5.) were "rancid" and grey, in diminishing degree. 6.) to 11.) inclusive were white and undecomposed. 12.) to 18.) also were undecomposed. (The serum in 17.) and 18.) was purple; due, no doubt, to the fact that these contain such a vast excess of acid.)

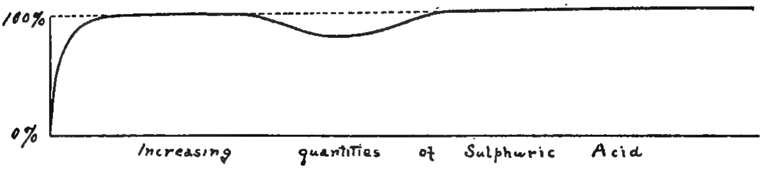
As the amount of hydrochloric acid increases, coagulation, which, with very small amounts of HCl is incomplete (taking as the time allowed a period approximately equal to the time which would elapse before the latex showed signs of natural coagulation or decomposition), becomes absolutely complete, and gives a clear serum; as the quantity increases further, coagulation is still complete; then a gap occurs—first the coagulation is incomplete, then there is no coagulation at all, and then again the coagulation occurs, but is incomplete—and, on the other side of the gap, the HCl can be increased indefinitely and will always produce complete coagulation.

Plotting roughly Completeness of Coagulation vertically—100% representing complete coagulation and 0% the complete absence of coagulation—and the Amount of Acid horizontally, a curve of the following general character is obtained.

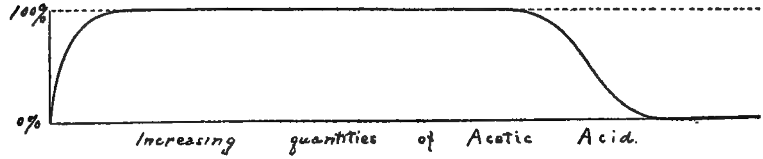
These curves are really all of the same type. A gap occurs over which no coagulation or incomplete coagulation only can be obtained. Apparently, the stronger the acid, the sooner is this gap reached; and, in the care of acetic acid, it is not bridged, as the amount of acid added increases. It is hoped to investigate the exact significance of the hiatus in these curves.



In the case of Sulphuric Acid the general character of the curve is as follows:



and in the case of Acetic Acid is follows:



SUMMARY

The analysis, which has been made in the foregoing pages, of the causes and conditions of natural coagulation in the latex of *Hevea Brasiliensis*, make it possible to understand more or less clearly the complex of processes which goes on when such latex is allowed to stand in the atmosphere. Briefly: a coagulating enzyme (not improbably a protease) is at work producing coagulation, which coagulation, however, is made difficult by dilution; anaerobic decomposition of the protein is going on, particularly in the parts away from the air; the oxidase Hevease is at work and may (depending upon the rate at which the changes occur and upon the condition of the medium as regards acidity) produce discolouration; aerobic decomposition sets in later, is most vigorous at the surface, and produces an alkaline slime which renders the liquid milky and accounts for the fact that latex allowed to coagulate naturally in the air never at any stage becomes clear.

That these four activities do not run parallel—certain of them predominating under one set of conditions and certain others of them under another set of conditions—shows them to be separate and distinct.

Some Cases of Degenerate Rubber

A number of samples of rubber which exhibit a particularly interesting degeneration have been encountered and examined. They show a gradual conversion of caoutchouc into resin and throw light, the author believes, on the rôle of caoutchouc in the physiological economy of *Hevea Brasiliensis.*

The samples originally encountered were crêpes prepared from the rubber which coagulates on the cuts. Six weeks after the date on which the rubber had been harvested, the resin-content of the samples was determined:

Sample 1	contained	26.8%
Sample 2	"	14.26%
Sample 3	"	9.94%

The samples were all "tacky," and of a rich brown color. Sample 1 was semi-fluid. The resins extracted were of a rich yellow-brown colour and had a smell like that of the original degenerate rubber and similar to that of the resin from normal Plantation Para.

Seven months later sample 1 contained 35.3% resin.

After 16 months sample 2 contained 71.3% resins, and sample 3, 78.02%.

As this increase in the resin occurred, the samples lost their "tackiness" and became shiny, smooth, and dry on the surface and, ultimately, brittle.

Later, a sample of No. 1 crêpe (weighing about 10 pounds), coagulated by acetic acid, and exhibiting a similar degeneration, has been examined more closely. Four weeks after the rubber had been harvested, it contained 6.59% of resin. It was of a rich brown color; was "tacky"; and had a smell similar to that of rubber resin. Ten weeks later the sample contained 19.08%

of resin; and the surface had largely lost its stickiness. The viscosity of this sample was extraordinarily low. Taking benzene as 1, the relative viscosity of a 1% solution was 1.23; of a .5% solution, 1.15; and of a .25% solution, 1.076. The viscosity of the rubber itself was thus about 230.[1] The viscosity of the normal rubber from the section of the estate in question is about 10,000; and that of a 1% solution more than 30.

Some investigations have been set on foot with the object of determining the cause of this degeneration. It is certainly not sunlight. The samples were not exposed to the sun during drying (they were found in the centre of a drying shed); and whilst under investigation have been kept away from the sun in a cupboard. Heat was never in question. The cause must therefore (in all probability) be some organic agency.

After the second resin extraction (giving 19.08%), some of the sample was cut up and its weight noted at intervals. Another portion was heated for half an hour at 100° in an air bath; was cut up; and its weight also kept under observation. The samples exposed approximately equal surfaces. In the course of 3 months the first sample increased in weight 4.38%, and the second sample 1.63%. It appears that the amount of heating to which the second sample was subjected did not entirely destroy the agency which is responsible for the conversion. The sample used in the above resin extraction was, after exhaustive extraction with boiling acetone, also kept under observation. The change of the caoutchouc to resin is going on almost as quickly as in the control. In 3 months the increase in weight was 3.29%. (This sample was kept in a desiccator.)

It has been mentioned that the samples are "tacky" in the early stages; but by no means all cases of "tackiness" are associated with the peculiar degeneration described above. Heat, either dry or moist, renders raw rubber soft and sticky without affecting any appreciable chemical change.

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[1] The viscosity of the rubber was calculated according to a slight modification (given by Schidrowitz, in a private communication to the author) of the method set out in Schidrowitz, P. and Goldsborough, H. A. The viscosity of india-rubber and india-rubber solutions, Jour. Soc. Chem. Ind., Jan. 15th, 1909.

Sunlight often has a similar effect; but prolonged exposure results in chemical change, as will be shown later. "Tackiness" in rubber collected from the ground around the tree or prepared from the bark shavings is probably occasioned by fermentative changes in the mass previous to cleansing. Specific chemical agents may produce the condition but only rarely.[1] Hydrochloric acid (as in 17 and 18, page 19), when in vast excess may; and sodium hydroxide often does. But the above types are not usually accompanied by any increase in weight or appreciable chemical change.

The case of sunlight is interesting and supports the idea to be advanced that, in the change of caoutchouc now under discussion, depolymerisation first occurs and is followed by oxidation. A sample of thick crêpe, with a normal resin-content of 2.63%, was exposed to the sun. After 3 months the rubber was very soft, but the resin-content of the part most affected had increased only to 3.23%. After 9 months, however, the resin-content of the part most affected had risen to 8.33%. The surface in this part had become dry, shiny, and smooth as in the degenerate samples earlier described. The resins were of normal appearance and small.

The case of a number of pieces of crêpe that have been found at different times to become "tacky in a few small areas only—these spots first have a green "mouldy" appearance—have been examined. It has been found that resins were high at this point, although normal over the rest of the sample. For example, one such sample had a resin-content, at a "tacky" spot, of 7.34%. These spots are now, after 14 months, dry and smooth and probably represent localised areas of the kind of degeneration earlier recorded.

The Conversion of Caoutchouc in the Tree

Of the suggestions that have been made as to the function of latex in the tree, the one that supposes it to act as a reserve food-stuff would have by far the greatest cogency, but for the difficulty of conceiving the conversion of caoutchouc into products assimilable by the tree. On the general ground that an oxidase is present in raw Para rubber, Spence, in his important paper,[1] suggested that the function of the latex was to serve as reserve food. But the oxidase recognised by Spence, and here called Hevease, acts, not on caoutchouc, but upon protein, and that caoutchouc could undergo conversion by enzymic activity remained purely an assumption. In the degeneration now under consideration, however, such a conversion of caoutchouc by (in all probability) enzymic change into an oxygenated product is actually seen in progress.

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[1] Rubber which had been immersed for 18 months in 25% HS_2O_4 did not become tacky when taken out of the acid and allowed to dry.

The ground from which the author views this change is the hypothesis that the caoutchouc is first depolymerised and is thus more easily oxidised than when in its ordinary state of aggregation.

The terms "depolymerised" and (as in the title of this communication) "depolymerisation" are here used in the loose sense which indicates merely a lowering of the state of aggregation. Strictly, polymerisation refers to a chemical change of the type in which a compound is converted into a more complex compound whose formula can be expressed empirically as a multiple of the empirical formula of the first compound; and depolymerisation should refer to a chemical change taking place in the opposite sense. It would be better in connection with rubber to abandon the term depolymerisation in the loose sense in which it is now used; since the term in question has implications as to the change to which it refers being a chemical one. The term disaggregation, which indicates nothing more than a lowering of the state of aggregation, would be preferable. At all events, what is indicated here is merely a reduction in the state of aggregation of the caoutchouc. That the disaggregation here in question—recognised, as it is, by the change in the viscosity—is only a physical or, at most, a physico-chemical, change, in the size of the caoutchouc aggregates, is sufficiently obvious.

It seems probable that any disaggregation of the caoutchouc

[1] Spence, D. On the presences of oxydases in india-rubber, with a theory in regard to their function in the latex. Bischem. Jour. Vol. III, 165.

in a sample of rubber renders the sample liable to become "tacky." It may be noted, in passing, that the great majority of cases of "tackiness" occur in the lowest grades harvested on a plantation. The rubber of these grades usually has a very low state of aggregation, as indexed by its viscosity.

Although it has been shown above that the conversion of caoutchouc by natural agencies actually takes place, the complete conversion of caoutchouc into simple products assimilable by the tree cannot yet be traced; but the actual existence of a change such as that into resin gives greater probability to the supposition that caoutchouc serves as a reserve food; for it is much easier to credit the break-down of oxygenated molecules such as those constituting resins into substances of value as foods than to imagine such a break-down in the case of the hydrocarbon molecule of caoutchouc. It is true that resins are not usually regarded as being re-assimilated by plants, and have frequently been, in a general way, ascribed protective functions or looked upon as excreted substances. The former of these functions is not likely to be more than subsidiary; and, as regards the latter idea: it is in large part little more than a confession of the meagreness of our knowledge of the part which resins play in plant physiology. It is quite possible for resins to be broken up into assimilable substances;[1] and it is reasonable to suppose that the conversion in plants of oxygenated products such as resins will be demonstrated and its course followed as the result of more prolonged and closer investigation.

That the utilisation of caoutchouc as a reserve food by a change such as that here posited possesses no *a priori* improbability is shown by consideration of certain general observations which have been made regarding the changes in latex at certain periods and in response probably to the tree's physiological exigencies. It has been noticed, for example, that the tendency to rapid darkening (on the cuts and in the cups) which has been shown (see page 4) to be due to exceptional enzymic activity, is particularly prevalent at the time of "wintering," especially when "wintering" is accompanied by drought. This was very striking in Selangor in March, 1911. Further, it is certainly worthy of remark that the largest number of cases of degeneration such as that discussed earlier were encountered at a time when the trees were both "wintering" and suffering from drought. This supports the hypothesis here advanced as to the conversion of caoutchouc in the tree; but without further data on this point it would not be wise to insist too strongly on this last fact.

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[1] See, e. g., Tschoich, A., Die Harze und die Harzebehälter.

The above observations show at least that the composition of latex as regards its enzymic constituents or as regards its enzymic balance can alter; that latex can behave abnormally under special circumstances; and that there is nothing improbable in the assumption that at the critical times at which, *ex hypothesi*, the caoutchouc is to be used as a reserve food, appropriate enzymic activity will be called forth. And it is to be noticed, as Spence has pointed out, that in latex the caoutchouc is in its lowest state of aggregation and, therefore, according to the present author's hypothesis, most susceptible to conversion.

Spence suggested [1] that in order to employ latex as a food the oxidases in the tree break it down into "simple carbohydrates-products of value as food stuffs." It is not improbable that such products are ultimately formed in the process of conversion of a reserve food such as caoutchouc; but, at all events, it seems probable that the first change in such a conversion is the formation of resins. Whether the normal percentage of resins (and of some other substances) in latex represents a state of equilibrium cannot yet be said.

The author wishes to acknowledge his indebtedness to the Directors of the Société Financière des Caoutchoucs for allowing him to publish these conclusions, and also to Mr. E. B. Skinner.

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[1] The viscosity of the rubber was calculated according to a slight modification (given by Schidrowitz, in a private communication to the author) of the method set out in Schidrowitz, P. and Goldsbrough, H. A. The Viscosity of India-rubber and India-rubber Solutions, Jour. Soc. Chem. Ind., Jan. 15th, 1909.

ADDENDUM

The author's attention has been drawn by Dr. K. Gorter to a memoir by the latter (*Mededeelingen over Rubber. No. II. Verdere Gegerens over het pekkigworden.* Door Dr. K. Gorter. Bintenzorg, 1912), in which are recorded results obtained regarding the production of tackiness in a Borneo rubber, by observations relating to its solar oxidation. These results appear to lend support to the hypothesis here advanced as to the necessity for disaggregation of caoutchouc to precede its oxidation; since they show the oxidation does not proceed immediately on exposure: there is an initial period of waiting before oxidation begins. Gorter explains the fact that the oxidation does not begin until the rubber has been exposed to the light for some time by supposing that the production of a catalyst is the first step; but the results would appear to be explained equally well, if not better, by the present hypothesis of an initial disaggregation. G. S. W., *August,* 1912.

As the original memoir here referred to is not easily accessible, Carter's results on the point here in question may be described. Some rubber from Borneo, deposited as a film on the walls by evaporation (by boiling) of its solution in benzene, was sealed up in a distilling bulb, arranged obliquely so that the outlet tube dipped vertically downwards into a vessel containing paraffin. The bulb was exposed to diffused sunlight; and the absorption of the oxygen in the bulb was followed by observing at intervals the position of the paraffin surface. During the first six days, no absorption of oxygen took place; the level of the trapping liquid then slowly rose and, after 20 days, had reached the top of the tube. The bulb was then opened, so as to admit air; and, after closing its bulb, the absorption of oxygen was again kept under observation. There was now no initial period of waiting: the surface of the paraffin at once began to rise, and reached the top of the tube in five days. The bulb was opened and then closed six times more; and the absorption of oxygen always proceeded at once, without any initial lag. Graphically representing the absorption of oxygen (vertically) with time (horizontally): the curve for the first period is at first horizontal and then gradually ascends; the curves for the subsequent periods are steeper and practically straight lines. The observations covered 60 days. The change in weight was very small. The presence of a little larerulinic aldehyde was recognized. Carter believes organic peroxides to be concerned in the reaction.

THE TECHNICAL PROBLEMS OF COAL PREPARATION

W. S. Ayres, C. E.
Hazelton, Pa.

(Prefatory Remarks made by the author in presenting his paper see Vol. X, p. 33.)

In presenting this paper, I desire to offer an apology for its brevity, particularly since it would require many volumes to record the whole history of the art, and still more so since conservative estimates declare that about 50% of the original deposit in the seams of coal is lost in the mining and in the process of handling and preparation, representing a loss that has run up into billions of dollars.

This enormous waste is a fair measure of the importance of this subject, and it must be frankly said that the problems as a whole have not yet been satisfactorily worked out, although material reductions in these losses have been made, and are still being made.

The science of chemistry gives us a field of facts that play a very important part in the art of coal mining and coal preparation, and must be employed continuously in perfecting the process.

But a discrimination must be made in its use, as applied to the mining end of the proposition, because the beds of coal are made up of seams of pure coal and comparatively thin bands of slate, and a chemical analysis giving fixed carbon, volatile matter, ash and sulphur tell the mine superintendent practically nothing because the free slate enters into the final result. On the other hand, a flotation test giving the percentage of free slate in the coal immediately tells him what is wrong with his preparation and enables him to trace the trouble at once, or it tells him that he must install improved machinery. The ash in the pure coal cannot be made any less by any process of preparation,—that is fixed by nature, and the market value of his coal in B. T. U. S.

is fixed by it also, but the free slate can be very materially reduced by a better preparation.

The consumer, however, finds valuable protection in the analysis of the coal he buys, particularly in steam sizes, yet I am strongly inclined to believe that so far as the determination of ash is concerned, that the flotation test for free slate, supplementing nature's fixed value, will give a far more satisfactory representation of the attainable purity of the coal and will avoid many disagreements.

THE USE OF NATURAL GAS IN STEAM BOILERS

George W. Barnes
Pittsburgh, Pa.

This use of natural gas is possibly the earliest in the history of this most valuable, yet, until a comparatively recent date, least valued fuel provided by nature, and in many localities the supply was seemingly inexhaustible with the natural result, the cost of installation was the only one considered and the efficiency was never determined, if even thought of.

The introduction of this valuable fuel into the commercial field did not for years suggest a reasonable valuation; millions of cubic feet daily were furnished to Pittsburgh and other localities, and sold to industrial plants for steam boiler use at a flat rate per H. P. rating, no attention being given to the installation or the quantity used, this being left entirely to the consumer, in fact many localities notably through the mid-continent field this practice prevails today.

As a result the types of burners and methods of installing were almost as numerous as the installations. Each engineer had his own opinion, and few, if any, based on either experience or knowledge of the use of gas or its application. A few of the novelties would not be credited today.

1. Rows of Bunson Burners under the shell (Return Tubular Boiler) starting at the front of fire box spaced eighteen inches apart extending the full length of boiler.

2. An open pipe flame in fire box and similar flame introduced at the back and driven into the tubes, the result being a red-hot stack at times of heavy load. The usual method of early installations being the perforated pipe burner introduced in various forms, this gave good results as a steam generator, but was extremely wasteful, some later tests showing an efficiency as low as twenty to twenty-five percent and few if any reaching fifty percent.

The first burners coming under the writer's observation designed for this work where a well defined knowledge of the requirements was apparent, was the "Whysall," this consisted of a series of well designed Bunson tubes, built into the side walls of the fire box, the flames striking across the fire box, meeting at the center where it was broken up, and any unconsumed carbon escaping the primary combustion was supplied with air admitted through the fire doors, making a practically perfect combustion of the gases before reaching the bridge wall. This type in various forms was used for several years and good results were obtained.

The type in use for the past ten or twelve years and one that has best met the requirement of the many varied conditions is the Tubular Burner. This is made in several forms differing only in minor details, and in fact has become the standard for Water Tube and Return Tubular Boilers. These burners are carefully designed and when properly installed give perfect results.

In installing care should be given to pipe and fittings, and ample capacity provided. This should be sufficient to supply the gas to the burner at a pressure of from three to five ounces, allowing for an overload of from fifty to sixty percent of boiler rating. In sketch will be found a good general plan of installation.

In operating it has been found that the best results have been obtained where the long straw white flame is used (note test made by Mr. Whitham for example) in addition the checker wall or a modification of same has been found absolutely necessary as the flame must come in immediate contact with an incandescent surface to insure a perfect combustion within the zone of usefulness. This system has been used almost exclusively for years.

While the use of natural gas for steam boiler work has not reached anything near the efficiency that has been obtained from its use in other industrial work or in domestic appliances, it by no means follows that it could not be greatly improved; in other industrial and domestic use furnaces and appliances have been designed and constructed best adapted to the use of gas, many having a sustained efficiency of eighty-five to ninety percent, while all steam boilers are constructed with a view to the use of coal as fuel and gas fuel not considered.

In the use of gas from seventy to seventy-five percent efficiency is about the maximum sustained.

In table of tests made at the West Virginia University under the directions of Prof. Clement R. Jones, a very practical result was obtained, and is a representative test showing what can be done in continuous work. By taking this test, and making allowance for difference in heat value of gas to be used, cost of steam can readily be obtained.

To compare with coal cost allowance should be made for the following items, in addition to coal on track, cost of handling to grate bar, ash removal, repairs, grate bars, linings, tube cleaning, (Return Tubular), boiler repair, over amount when gas fired, cleaning machinery—resulting from coal and ash dust, additional oil, from same cause, value of overload, short or long, possible with gas, value of automatic regulation and constantly uniform steam pressure under all loads, all this should be determined and added to cost of coal or deducted from cost of gas before you can fairly and accurately compare the relative cost.

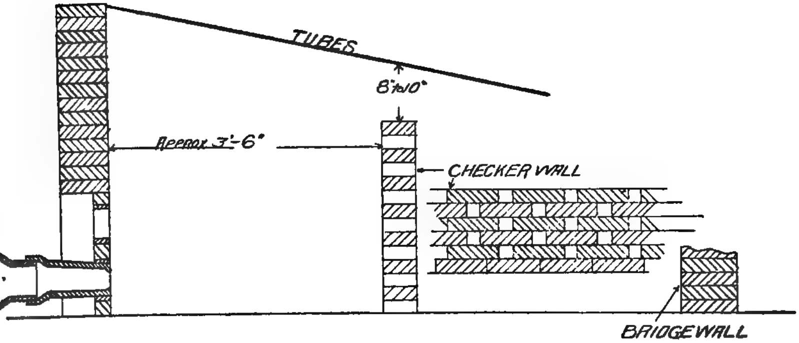
Note—The writer in preparing the above had in mind only the briefest sketch of the subject, and treated it in a general way, not deeming it desirable to go into detail, as this would require as many various applications as there are plants, as no two can be installed the same in all details, location of plant with reference to physical surroundings, conditions of fire room, stack draft, nature and type of boilers, setting, constant or variable load, and last but not least the type of man and his preferences, who superintends your steam plant, all must be considered in making a success of the use of gas, and can only be treated individually.

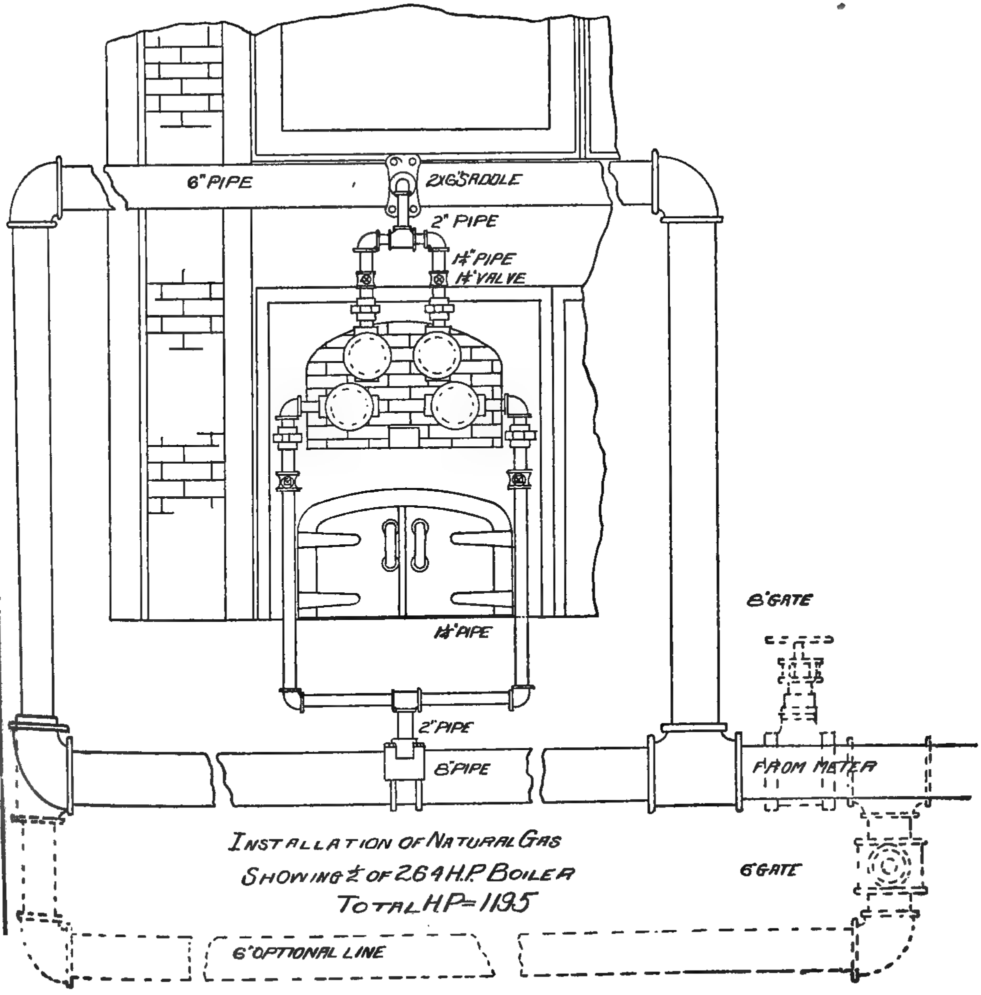
Any details, tests or data that the writer may have or any suggestions are at the disposal of the readers.

EXTRACT FROM PAPER PREPARED FOR THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS, BY JAY M. WHITHAM, IN WHICH HE GIVES THE FOLLOWING SUMMARY OF SIX TESTS MADE IN WATER TUBE BOILERS

Kind of flame	White	Blue
Number of 250 H. P. Boilers used	6	6
Average gas pressure at burners ounce	6	6
Cu. ft. of gas used when reduced to 4 ounce and 60°F	626815	561638
Equivalent water evaporated at and from 212°F	496163	441963
Average boiler H. P. made	1597.7	1423.2
H. P. made per 250 H. P. boiler	266.3	237.2
Cu. ft. of gas reduced to 4 ounce pressure and 60°F. used per boiler H. P. per hour	43.6	43.8

Showing that the economy is the same with each and that the capacity is greatest with the white flame.





INSTALLATION OF NATURAL GAS
SHOWING ½ OF 264 H.P. BOILER
TOTAL HP=1195

WEST VIRGINIA UNIVERSITY ENGINEERING LABORATORY

Tabulated Results of Gas Burner Tests

1	Number of Test	1	2	3	4	5	6	7	8	9	10	11	12	13	16	17	18	19	1
2	Date of Test	1/27/06	2/10/06	2/13/06	2/16/60	2/17/06	2/22/06	2/23/06	2/24/06	3/3/06	3/10/06	3/16/06	3/17/06	3/24/06	5/10/06	5/11/06	6/8/06	6/9/06	2
3	Duration of Test in Hours	5	5	3	5	5	5	5	4	5	5	4	5	5	4	5	5	5	3
4	Color of Flame	Colorless	Colorless		Colorless with Blue streaks	White with Blue streaks	White with Blue streaks	Colorless		White	Colorless	Colorless	Colorless	Colorless				Colorless	4
5	Pressures																		5
6	Steam Pressure in Boiler by Gauge	120	120	121.5	121	122	123	122.5	121.5	120.5	121.5	121.5	120.5	121.0	120.5	121.0	120.0	119.5	6
7	Gas Pressure in Ounces, above Atmosphere	7	5	8	5	8	3	8	3	8	3	6	3	3	3	4.78	8	8	7
8	Gas Pressure in Inches of Mercury	.9	.64	1.0	.64	1.0	.4	1.0	.4	1.0	.4	.76	.4	.4	.4	.61	1.0	1.0	8
9	Draft in Inches of Water	.15	.15	.45	.45	.45	.44	.48	.50	.40	.45	.40	.43	.47	.40	.40	.30	.35	9
10	Atmospheric Pressure by Barometer	29.10	29.51	29.15	29.54	29.35	29.26	29.16	29.15	28.66	29.00	29.04	29.32	29.63	29.28	29.35	29.06	29.00	10
11	Temperatures in Degrees Fahr.																		11
12	Of Feed Water	45.5	39.0	40.0	38.4	38.0	37.9	38.9	38.3	41.2	41.5	40.0	40.0	40.0	57.0	57.0	69.0	70.0	12
13	Of Gas at Meter	53.8	48.0	49.0	47.4	48.3	48.7	50.4	48.9	51.5	50.5	46.5	48.3	48.6	62.0	63.3	73.2	76.3	13
14	Of Flue	239	229	261	250	269	273	273	279	265	262	262	269	267	245	250	207	213	14
15	Of Boiler Room	64.4	53.0	66.5	59.8	69.0	68.0	75.5	74.5	75.8	69.5	63.0	68.0	70.0		83.0	86.4	93.0	15
16	Pounds of Water Evaporated per Hour from and at 212° Fahr.	4151	2861	5711	4734	6248	6003	6390	6600	6010	6075	6686	6399	6327	3778	5244	3909	4086	16
17	Quality of Steam in Percent	85.0	80.0	89.0	86.7	93.0	96.0	97.0	96.5	96.3	95.6	95.8	96.1	94.7	82.0	93.5	81.4	80.2	17
18	Boiler Horse Power	126.0	89.0	172.6	142.7	184.7	175.9	186.5	193.2	176.0	178.9	196.0	187.5	186.2	116.1	155.0	120.5	126.2	18
19	Cubic Feet of Standard (32°F–29.95) Gas per Hour	5632	4204	7247	6126	8044	7185	8109	8593	7999	7672	8698	7209	7116	5121	7212	5585	5778	19
20	Cubic Feet of Standard Gas per Pound of Water Evaporated from and at 212°F.	1.35	1.47	1.27	1.29	1.28	1.19	1.26	1.30	1.31	1.27	1.30	1.12	1,12	1.36	1.37	1.43	1.42	20
21	Cubic Feet of Standard Gas per Boiler Horse Power	44.4	41.1	42.1	42.8	43.5	40.8	43.4	44.4	45.4	42.8	44.3	38.4	38.2	44.1	46.5	46.3	45.8	21
22	Total British Thermal Units per Cubic Foot Standard Gas	1110	1143	1144	1098	1156	1143	1116	1029	1124	1108	1071	1134	1136	1100	1100	1037	1088	22
23	Available British Thermal Units per Cubic Foot Standard Gas	1040	1060	1056	1015	1056	1064	1039	992	1046	1018	983	1032	1050	1031	1031	918	955	23
24	Efficiency of Boiler in Percent	67.1	61.9	69.2	71.0	66.0	71.2	68.8	70.7	65.3	70.2	70.2	76.7	76.8	68.6	65.8	69.4	66.9	24
25	With, or Without, Steam Jet in Burners	With	With	Without	Without	Without	Without	With	With	Without	Without	With	With	With	Without	Without	Without	Without	25
26	Flue Gas Analysis, Percent by Volume																		26
27	Carbon dioxide—CO₂	8.90	6.80	8.20	7.70	8.50	8.20	8.96	8.07	8.00	8.26	9.26	8.00	8.53	6.52	8.00	8.40	8.80	27
28	Oxygen—O	4.30	7.10	4.50	6.80	3.70	4.70	3.60	3.60	2.70	4.06	4.26	6.00	5.13	8.90	3.00	4.60	4.40	28
29	Carbon monoxide—CO	0.00	0.40	0.10	0.00	0.30	0.23	0.08	0.83	1.70	1.00	0.56	0.00	0.00	0.00	1.00	0.00	0.00	29
30	Nitrogen—N	86.80	85.70	87.20	85.50	87.00	86.87	87.36	87.50	87.60	86.68	85.92	86.00	86.34	84.58	88.00	87.00	86.80	30
31	Excess Air	22.8	45.3	24.1	42.7	18.9	25.4	18.3	18.2	13.0	21.3	23.0	35.4	28.7	65.5	14.6	24.7	23.4	31

AMERICAN OIL SHALES

CHARLES BASKERVILLE AND W. A. HAMOR
College of the City of New York, New York, N. Y.

In several communications by the authors on the economic value of the oil shales of Canada[1], it was shown that the beds of oil shale in New Brunswick are very extensive, that the principal by-product obtained on retorting (under suitable conditions) ammonium sulphate, will often more than bear the expense of mining and treatment, and that the crude oil obtained by retorting New Brunswick oil shale is essentially the same as the petroleum of the mid-continent field. The importance of these large deposits of fuel oil has been appreciated, for a strong company, The New Brunswick Shale Co., Ltd., capitalized at $5,000,000 has been organized for their development. The formation of this Company and the doubtless early working of the New Brunswick shale deposits, have aroused much interest in other parts of the Dominion, especially in New Foundland, Nova Scotia, and Ontario, where other oil shales occur, as well as in the United States.

The commercial success and tribulations of the shale oil companies now in operation in Scotland are well known[2]. The oil shales in the Wolgan and Capertee valleys, New South Wales, Australis, and at Autun and Buxiere-les-Mines, France, are also being worked. While the Orepuki, New Zealand, and Camamu Basin, Brazil, oil shales were found, upon being worked, to be low-grade and to require high development charges, and although a company is being organized to acquire the oil shale properties situated near Ermelo in the Transvaal, the authors are unaware of any large operations on the oil shale deposits of Spain, Austria-Hungary, Turkey, Tasmania, Mozambique,

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[1] Proc. Seventh Internat. Cong. Appl. Chem., 1910, Section IV al; Eng. Min. J., *88* 149–54, 195–99; J. Ind. Eng. Chem., *1*, No. 8, (1909).

[2] See Ells and Hamor, Canada Department of Mines, Report No. 55, Mines Branch, Ottawa, 1910.

Natal, Italy, and the United States for the production of crude oil and ammonium sulphate. In this country from 1854 to 1860, various bituminous materials were distilled for the production of illuminating oil by fifty-five "coal oil" companies, but the process followed was very crude and ammonium sulphate recovery was never attempted. Consequently, although many of the coals and other materials used were of high grade,[1] and merit investigation as to yield of oil, gas, and ammonium sulphate according to modern practice, it is not surprising that the discovery of petroleum paralyzed the industry. However, interest in the deposits and raw materials of more or less similar properties, is awakening.

In the United States, oil shales[2] occur in Kentucky; on the Humboldt River, opposite to Elko, Nevada; on the Big Blackfoot River and near Great Falls, Montana; and in the Cholame Valley, north of Parkfield, California. Some of these are of good quality, but none has been worked to any extent. It is likely, however, that the incerasing demand for liquid fuel and ammonium sulphate may occasion a thorough investigation of these deposits. Some time ago the authors examined a sample of oil shale from Montana. This shale was friable and blaey, being weathered; it yielded 41.5 pounds of ammonium sulphate and 6 gallons of crude oil per short ton.

Some carbonaceous shale is being used in the manufacture of paint in the United States, but in the processes employed the nitrogen present is not recovered.[3]

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[1] See Baskerville, Eng. Min. J., *88*, 151.

[2] Reference is had here to shales which contain an *oil-forming* substance, kerogen, which gives rise to oily and tarry matters on destructive distillation; and not to *oil-bearing* shales, from which petroleum may be obtained by mechanical means.

[3] The Nashville Carbon & Oil Company, of Nashville, Tenn., are producing a "natural carbon" paint ("Durbon") from shale; the raw material is heated in air-tight retorts, and from 8 to 10 gallons of crude oil is produced from one ton. Both the dark oil and the black residue are used. The Natural Carbon Paint Company, of Freeport, Ill., formerly mined carbonaceous shale both in Mt. Carroll and Eleroy, Ill.; this was distilled in special retorts, and black carbon pigment, shale oil, and gas were obtained as products. The shale oil was said to contain a large percentage of ichthyol, but it was not utilized,

The oil shale deposits of America constitute a fertilizer well as a fuel resource of decided economic possibilities. However, the methods by which these resources may be utilized with greatest profit, require careful inquiry.

the manufacturers operating the plant having been only interested in the production of a pigment suitable for what was regarded as an anti-corrosive and steel protective paint. For two years, up to November 1, 1911, the plant was operated by a Chicago paint Company.

THE EXTRACTION OF GASOLINE FROM NATURAL GAS

George A. Burrell and Frank M. Seibert
U. S. Bureau of Mines

Present methods of extracting gasoline from natural gas are described, and the principles upon which the industry rests explained.

Analyses are shown of natural gases from which gasoline is extracted upon a commercial scale.

Tests are described which can be used to determine the adaptability of different natural gases to gasoline manufacture.

The handling of the gasoline and factors which determine the yield are discussed.

COMPOSITION OF SOME NATURAL GASES

George A. Burrell and Frank M. Seibert
U. S. Bureau of Mines

The composition of natural gases from different parts of the United States is shown. Heating values are included. Methods of analysis are described in detail. The natural gases described consist of paraffin hydrocarbons, carbon dioxide and nitrogen; in two cases hydrogen sulphide was detected. Errors which arise due to the use of ordinary methods of gas analysis in examining natural gases are explained.

METHODS AND REASONS FOR ANALYSES OF BITUMINOUS MATERIAL BY THE MASSACHUSETTS HIGHWAY COMMISSION

H. W. Clark and George O. Adams
Boston, Mass.

For the past four years analyses have been made of samples of all the bituminous materials used in road work by the Massachusetts Highway Commission. During this period approximately 1,350 samples have been examined and many investigations in regard to methods of analysis, etc., have been carried on. The chief aim in the routine laboratory work has been to show clearly and by the smallest possible number of the most reasonable and common sense methods of analysis, the general character of each material used, its uniformity of composition as bought, shipped and used at different portions of the State at different times and throughout different seasons, and the relation in various important physical and chemical characteristics that each binder used bears to each other binder. It is only by such work in connection with road observations by the Commission in regard to the lasting qualities of the road built, that a basis of knowledge can be gained that will show with some degree of certainty the value of the different binders and different methods used.

At the present time our tests as made upon tars and asphaltic bodies are as given on the following pages. The way in which these tests are carried out probably differs but little from the procedure in many other laboratories.

Trade Name of Sample Chemist's Sample No.

	Tars	Asphalts
Specific Gravity		
Viscosity 100°C., Lawrence Viscosimeter	seconds	seconds
Penetration 20°C., Dow Penetrometer		

Insoluble in Carbon Bisulphid (Free carbon)		per cent.	per cent.
Insoluble in 88°B. Naphtha		"	"
Fixed Carbon		"	"
Paraffin		"	"
Evaporation	12 hours at 100°C. (Tar)	"	
	12 hours at 250°C. (Asphalt)		"
Distillation	Up to 105° C.	"	
	105° to 170° C.	"	
	170° to 225° C.	"	
	225° to 270° C.	"	
	270° to 360° C.	"	

METHODS OF ANALYSIS USED FOR BITUMINOUS MATERIALS

Specific Gravity. About 20 c.c. of the warmed sample is poured into a weighed 25-c.c. graduated flask and allowed to stand for several hours at 70°F. The flask is then weighed and filled with distilled water at 70°F. and suction applied to the neck of the flask to remove air bubbles in the sample. The flask is then made up to the mark with water and weighed. A simple calculation gives the weight and volume of the sample, and from these, the specific gravity is calculated.

Viscosity. Viscosity is determined by noting the seconds required at room temperature for 60 c.c. of the sample to pass through the Lawrence viscosimeter at 100°C. The water jacket of the viscosimeter is heated to boiling and the sample previously heated to 100°C. is strained through wire gauze into the pipette of the viscosimeter. The 60 c.c. is measured by collecting a weight equivalent to 60 c.c.

Penetration. Penetration is determined by the Dow penetrometer using 100 grams load. The sample is melted in a three-inch tin dish and cooled to 20°C. The penetration of the needle into the material in 5 seconds is measured and expressed in units of 1 $\frac{1}{100}$ c.m.

Per Cent. Evaporation. The per cent. evaporated is obtained by weighing about 20 grams of the sample into a weighed flatbottomed tin dish three inches in diameter and heating for twelve hours at 100°C. in the case of tars, and 250°C. in the case of asphaltic compounds. After cooling, the dish is weighed and the per cent. lost calculated.

Per Cent. Insoluble in Petroleum Ether and Carbon Bisulphid. Five to ten grams of the sample are weighed into a weighed extraction shell and then extracted in a Soxhlet apparatus until the solvent is colorless. The shell is then dried and weighed in a weighing beaker. In case of asphaltic compounds the portion insoluble in carbon bisulphid is found by extracting the portion insoluble in petroleum ether.

Distillation. Distillations of tars are made in the usual way in an iron retort as described in various places.

NOTES IN REGARD TO METHODS

Besides the tests which we are in the custom of carrying out in this laboratory with each sample, various other tests and methods have been proposed from time to time by different analysts working along this line. Some of these will be referred to later. Each of the tests that we carry out is intended to show some characteristic of the body under examination that it is desirable to ascertain.

Specific gravity, for instance, shows the density of the material and hence gives a clue indirectly to the amount of bitumen present. With tars a high specific gravity indicates a high percentage of free carbon and vice versa. Low specific gravity of an asphaltic body occasionally indicates bitumen of a particular character. Oils of the same viscosity but from different oil fields may have quite different specific gravities and again if two oils from the same source are of the same viscosity, the one which has been "blown" will have a lower specific gravity, generally speaking, than the one which has been formed from solid asphalt. The form of apparatus that we use in making this test as described above, is cheap, easily freed from air bubbles and easily cleaned by carbon bisulphid followed by hot alkaline permanganate.

In the determination of viscosity a number of forms of viscosimeters are in use, the one used by us being a modification of the Engler viscosimeter and better suited in our judgment to the examination of heavy asphaltic oils and tars. The consistency of samples which are not sufficiently fluid at 100°C. to flow through the viscosimeter is determined by the penetrometer. This measures the distance which a standard needle will penetrate under a given load. This determination has a certain value but it has been found by us that the penetration figure of a number of samples from the same source may vary 50 per cent. or more and yet other factors, such as specific gravity per cent. of the material insoluble in 88° naphtha and the per cent. that will evaporate in the evaporation tests, be practically identical. The difference in penetration probably shows, however, some difference in composition of the different material not shown by the other tests, and road observation may in time give some information gained by this test.

The asphaltene determined by the per cent. insoluble in 88° naphtha is in residual oils probably due to polymerization caused by heating the body during manufacture. Its presence increases the consistency of an oil but it is perhaps not a desirable component. In some laboratories this body is determined by treating a portion of the sample for some time with 99° naphtha and then collecting the insoluble portion on a Gooch filter. This method is in our opinion tedious and duplicate results hard to secure. In this laboratory it is determined by placing the portion of the material under examination in a double-thick extraction cartridge in the usual Soxhlet extractor. The naphtha is not cold to be sure, but the only heat is that radiated by the oil bath in which the extractor flasks are heated. One objection to this method is perhaps that the lighter portion of the naphtha is volatilized and lost. This is not serious as duplicate results can be obtained without difficulty. The extraction cartridges are weighed in glass-stoppered weighing beakers on account of the readiness with which they absorb moisture.

Determinations of free carbon are also made in the Soxhlet extractor using carbon bisulphid as a solvent. It is probable, however, that none of the oils or asphalts examined contain free carbon, the portions that we have found insoluble in carbon bisulphid being mineral matter, dirt, etc.

The percentage of a sample that evaporates when the sample is heated under differing conditions, shows to a certain extent whether an oil has been "blown" or has been made by "fluxing" a solid asphalt with a low boiling flux. That portion of the binder that will evaporate at a comparatively low temperature will certainly be of little use on the road. This test in the case of tars, gives a clue to the extent that the tar has been refined. The proper degree of heat to which to carry on this test, is a matter of doubt and apparently should vary with different classes of samples.

Paraffin is determined by the Saybolt method, so called, given on page 556 of Richardson's "Modern Asphalt Pavement." It is not a particularly satisfactory method as the paraffin is separated from the non-volatile portions by destructive distillation and during this distillation, paraffin might be formed from the decomposition of other bodies. On the other hand, paraffin originally present is undoubtedly decomposed during distillation. This has been clearly shown by us by distilling some ordinary commerical paraffin when a considerable volume of gas, liquid and residue were obtained together with solid paraffin.

With tars it is customary to make fractional distillation as in other laboratories. So far as is known, however, it has never been shown that any one portion of the distillate is of any more value or of any more harm than another when these tars are used for road purposes.

We have made a number of determinations of the water soluble materials, both organic and inorganic, as recommended by the Special Committee of the American Society of Civil Engineers, but in no case have we found more than one or two tenths of a per cent. of total water soluble material. It has seemed, therefore, that this test was not worth making.

The same committee recommends a determination of the solubility of the body in cold carbon tetrachloride. According to Richardson, "the hydrocarbons and their derivatives" which are soluble in carbon bisulphid but not in cold carbon tetrachloride, should be known as "carbenes." As a matter of fact, however, whenever we have tested with carbon tetrachloride, we have obtained practically the same results as with carbon bisulphid, that is, we have not found "carbenes."

The determination of fixed carbon is also recommended by that committee. Fixed carbon is the carbon which any bituminous material will yield when heated to a high temperature in the absence of oxygen. It is practically coke, that is, the carbon remaining from the decomposition by heat of the various hydrocarbons forming the bitumen. There seems to be little reason for making this determination and the method of determination given by the Special Committee is one with which it is almost, if not quite impossible, to obtain duplicate results.

We have as yet seen no reason given for determining the melting point, so called, as has been recommended.

As stated in the beginning of this article, the laboratory work as a whole is intended to show as clearly as possible and with the least number of tests, the important physical and chemical characteristics of the material undergoing examination, tests which the engineer will understand and tests which will satisfactorily compare one material with another. All of the tests that we consider of practical value from our investigations so far made, are included in our routine work described above. These tests can be made with a reasonable degree of celerity and the results forwarded to the engineers without undue delay.

(*Résumé*)

LES EMPLOIS INDUSTRIELS DU COKE DE GAZ EN FRANCE

M. Henry Decluy
Ingénieur, Chef du Service Technique du Comite Central des Cokes de France

L'auteur expose, dans son préambule, les conditions économiques qui déterminèrent la création du Comité Central des Cokes de France, qui prit l'initiative de toute une série de travaux techniques sur l'utilisation du coke de gaz dans l'industrie: production de la vapeur, gazogènes pour les traitements thermiques de métallurgie, gazogènes à gaz pauvre pour la production de force motrice, utilisation du coke dans les industries de la chaux, des ciments, du plâtre, du sucre, chauffage central, appareils de chauffage domestique, etc.

L'auteur a dû limiter sa communication à l'étude de l'emploi du coke pour la production industrielle de la vapeur. Après avoir donné les définitions du pouvoir calorifique, adoptées par le Comité Central des Cokes de France, et indiqué une méthode rapide de détermination du pouvoir calorifique utile des cokes, il étudie les générateurs à grilles fixes brûlant du coke de gaz et donne des indications précises sur les conditions de la combustion et la conduite des feux, sur le meilleur mode d'utilisation des divers conditionnements du coke. Ensuite, il passe à l'étude des foyers soufflés à grilles fixes et à grilles mécaniques; il décrit la Grille roulante auto-décendreuse de la Société "Underfeed Stoker," qui fut l'une des seules en France à donner de très bons résultats dans l'emploi du coke.

En ce qui concerne l'usure des générateurs qui emploient le coke de gaz, l'auteur démontre l'inanité des craintes qui se sont manifestées, et cite des observations typiques faites sur des chaudières qui brûlent uniquement du coke depuis plus de 20 ans.

Enfin, dans un dernier chapitre entièrement consacré aux résultats obtenus pour la production de la vapeur, il relate ceux qu'obtient depuis trois ans, dans ses usines municipales, la Ville de Paris, et donne le détail de séries d'essais industriels, tous faits dans des conditions différentes de calibrage de combustible, soit en tirage naturel, soit en foyer soufflé, sur grilles fixes ou sur grilles mécaniques.

De cette étude très complète se dégage l'intérêt considérable que présente le coke de gaz comme combustible de générateur.

TECHNICAL APPLICATIONS OF VISCOSITY

Albert Ernest Dunstan and J. F. Strevens
East Ham Technical School, London, England

At the seventh international congress of Applied Chemistry, London, one of the present authors, (Dunstan, Section 10, p. 163,) foreshadowed the more extensive application of viscosity as a valuable constitutive property, not only because of its specific suitability as a criterion of lubricating efficiency, but also as a means of determining adulteration and checking purity. It is indeed a matter for astonishment that a property which varies within such wide limits for individual substances, and which with properly designed apparatus, is so susceptible to accurate measurement should have met with so little application in technical chemistry.

In this communication, which deals more particularly with the connection between viscosity and lubrication, the authors desire to advance the proposition that the viscosity of a lubricating oil can only satisfactorily be dealt with in the form of a temperature curve, so that the behaviour of an oil can be approximately predicated knowing the working conditions, for although it is true that a good lubricating oil will and does prevent friction, and keep down the temperature of the bearings and moving parts, yet if the normal conditions are such that an apparently good oil acquires a negligible viscosity, then of course it fails in its specific function, and undue heat is developed. Further they wish to point out that the viscosity of an oil should be expressed in absolute units of dynes per sq. centimetre so that all oils may be *directly* compared, and lastly that the apparatus in which the bulk of the purely scientific work in viscosity has been carried out is eminently suitable for technical work.

Hitherto the application of viscosity to determine the suitability of an oil for lubricating purposes under certain conditions has been confined, in most cases, to the comparison of rate of flow for a given volume of the oil in question under the same conditions of temperature and pressure (head), from a standard viscometer. Results so obtained may be expressed as, (a) seconds for outflow at a certain temperature, or (b) a ratio number compared to a standard liquid at a stipulated temperature as unity, such as rape oil, sperm oil, tallow, water, glycerin solution etc.

Oils in common with most other liquids, suffer appreciable reduction in viscocity on subjecting them to increasing temperatures, more so than ordinary viscometers indicate, when one considers the largely decreasing density with rise of temperature. The change in viscosity depends primarily on the original constitution of the oil, secondly on its content of dissolved solid matter, and also on the changes accruing in the oil at the temperature of the determination. (All oils are here considered without moisture and suspended solid matter, which act mechanically in giving erroneous results).

EVOLUTION OF VISCOMETERS

The oil dealer of mid-Victorian times was content to judge the body of an oil by comparing the time taken for complete inversion in a bottle, against an oil which had previously proved suitable for his purpose in a similar bottle. In 1850 Nasmyth, (*Mechanics Magazine*, 1850, 1, 111, 313,) introduced a rough comparison apparatus, consisting of a plate of iron with similar longitudinal channels in it. The plate was fixed at a certain angle, and the oils to be compared were simultaneously poured in equal quantities out of a row of small brass tubes into the upper ends of the grooves, and the time of flow along the channel carefully noted. The apparatus was subsequently improved by Albrecht, (Die Schmiermittel). Pipette and burette viscometers have been used and devised from time to time, but were very inaccurate, owing to the great difficulty of standardising and keeping constant temperature. Schubler carried out the earliest experiments in a glass tube 2 cms. diameter and 10 cms. high with a narrow tube attached of 1.6 mms. diameter. He divided the number of seconds required for water at the same temperature, and obtained a ratio which he called the specific viscosity. Other viscometers on the same empirical plan, but jacketed, have been devised by Lacker, McIvor, and Veitch Wilson. But the figures obtained from one instrument were not capable of conversion into those yielded by others, or even comparable. Napier (Glasgow) first devised an apparatus where the "head" of oil was kept constant and regulated according to the density of the oil being examined. Mason, (*Chemical News*, Oct. 31st. 1884) afterwards introduced an improved form of the same instrument. Cockerill introduced a viscometer on an entirely new principle in which a small paddlewheel was caused to revolve till it reached a uniform speed, by means of a falling weight, and the number of seconds taken for this weight then to fall a certain distance expressed the viscosity of the oil. On account of serious frictional errors which were introduced, different apparatus could not be constructed to give identical results. To avoid the irregularities and discrepancies due to the use of such forms of viscometer Sir B. Redwood introduced in 1885, his improved instrument, which has become the standard apparatus used in determining oil viscosities in this country. He proposed to make specific gravity corrections on the following formula,

$$\text{Viscosity} = \frac{N \times 100 \times S}{535 \times .915}$$

N = the number of seconds required at 60°F. for 50 ccs. of oil to flow out, S = the sg. of the oil at 60°F. Rape oil taking 535 secs. at 60°F. and having an s.g. of .915 at that temperature, being considered as 100. The correction is only applied, we believe, in very rare instances, observers being content merely to state the number of seconds of outflow for 50 ccs. of the oil at the temperature of the experiment. Owing to the excessive amount of radiation from the heated liquids at temperatures from 150° to 250°F., results at these temperatures vary considerably. Different experimenters use different methods for taking a high temperature viscosity, some being content to run their oil from the instrument at a high temperature into the 50cc. flask at room temperature, whilst others run the oil into the bottle immersed in a bath at the same temperature as that of the observation. Allen's modification of Redwood's apparatus, whereby a constant head of oil was maintained at a definite temperature, thereby ensuring a steady flow of oil, is described in Allen's Commercial Organic Analysis, in the oils and fats division. Engler's viscometer, the standard instrument in Germany, is a similar instrument to the Redwood. Engler and Kunkler, (Jour. Soc. Chem. Ind. 1890, 654.) designed a viscometer for the examination of oils under high constant temperature. Kunkler, (Dingl. Polyt. Journ. 290, 281,) described a viscometer in which only 30 cc. of oil are necessary. The Saybolt viscometer, as used by the Standard Oil Co., and its offshoots, is not obtainable in commerce. A description appears in Redwood's Petroleum, Vol. 2, p. 608, and in Lewkowitsch, Oils, Fats and Waxes, Vol. 1, p. 270. Kunkler (Chem. und Techs. Zeitung 11, No. 21, pp. 670–672,) devised an instrument, (Redwood, Petroleum 2, pp. 613–614,) made of brass and immersed in a constant temperature bath, for comparing the relative consistency of greases by their rate of flow under a given temperature (50°C) and pressure. The comparative viscometers of Arvine, Barbet, (ixometre), supposed to be more sensitive than an ordinary jet viscometer, and maintaining a constant head of oil, Lepany, Gibbs, etc. are described in Redwood's Petroleum, (Vol. 2, pp. 618, 619.)

Traube, (Journal Soc. Chem. Ind. 1887, 414) condemns comparison viscometers of the above type, on the ground that, theoretically, it is not permissible to compare the respective times of delivery of heavy and light oils, or oils and water, observed in one and the same apparatus, owing to the important effect played, by the formation of eddies and kinetic energy of efflux and surface tension.

Petroff (Grossmann, Die Schmiermittel, pp. 42–49) proposed to determine the actual viscosity in absolute units (i. e. the internal friction of the molecules) at working temperatures and found the very important relation that the order of the oils with respect to their absolute viscosity at a given temperature was the same as that of their lubricating powers.

The subject was again taken up by Archbutt and Deeley, (Lubrication and Lubricants, article Viscosity) who designed a convenient viscometer and measured the specific viscosities of oil and glycerin solutions.

The temperature of a bearing surface is liable to vary considerably within rather wide limits in actual practice; hence it is important to know the viscosity changes that are likely to take place in the interval (independent of any chemical action due to external influences).

For relatively low temperatures (70°F to 250°F) an indication only of such changes is obtained by using any one of the standard instruments now in use, but for temperatures ranging from 250°F to 500°F. which are often reached in the lubricated parts of internal combustion engines and steam cylinders, no information has hitherto been available. By plotting seconds of outflow obtained in a Redwood against temperature in a range of say, 150°F to 300°F, and extrapolating the most probable curve from the result, a straight line approximately parallel to the axis is obtained, and varying within extremely narrow limits, tending to show that, no matter what was the original condition of the oil, all viscosities tended towards the same minimum as the 300° to 600°F was reached.

All liquids, no matter how mobile, and even gases, possess some internal friction which is capable of accurate measurement. Lewkowitsch is of the opinion that it would be too tedious to use apparatus having capillary efflux tubes for estimating the viscosity of oils, but this is not the experience of the authors, who use the below mentioned type and prefer it to the ordinary methods.

The apparatus as indicated in the diagram, was about 15 cms. long the capillary being about 6 cms. by 1mm. diameter.

In using, the instrument is suspended vertically in an oil bath, (for high temperature work a bath of ceresin and white mineral oil is preferable, as it does not quickly discolour) allowed to remain in it about ten minutes, to attain the desired temperature, in all cases obtained by a motor driven propellor and stirrer, and then filled to the level marks c, d, with the oil under examination, thus allowing a constant head of liquid for all temperatures. After standing a further ten minutes, the oil, now being at the same tempertaure as the bath, is sucked up into the limb A above a, and the time of flow between a and b taken, about six times, and the mean accepted as the actual rate of flow. It is necessary that the density be also known, at the temperature of the observation, and this is obtained from a density-temperature diagram in the following manner, A glass specific gravity bottle is calibrated with pure distilled water from 15°C to 99°C, by first finding the actual weight of water it contains at intervals of 20°C in the range 15° to 100°C. This is obtained by weighing the bottle and water after it has been allowed to reach the desired temperature in a water bath fitted with an accurate thermometer and stirrer. The actual volume of one gm. of water at temperatures from 20°C to 100°C is obtainable from any book of physical chemical constants, and hence the actual volume of the s. g. bottle can be calculated and by plotting a curve and extrapolating, its actual volume at any temperature can be obtained.

When determining viscosities and densities simultaneously, the bath consisted of a Jena glass beaker containing the liquid which was heated by a Bunsen burner. The stirrer, viscometer, s. g. bottle and thermometer were suspended through an aluminum lid. For high temperature work no thermostat was used. The density bottle was kept at constant temperature for five minutes, levelled off to the mark, cooled and weighed. By observing the oil in the viscometer as the temperature rises, the actual decomposition point can be noted. If necessary a density curve can be obtained independently at temperatures other than those at which the viscosity is being determined, and the actual densities at the required temperature obtained from the curve.

It is essential that a standard liquid whose viscosity is known, and which has a measureable time of flow in the instrument under consideration, and which can be obtained quite pure, should be used for calibrating the viscometer. The liquid used was phenol which was carefully purified by distillation. Its time of flow and density were taken through a range of temperature from 45°C to 150°C. From the curve connecting phenol viscosity and temperature, the constant for the oil viscometer can be obtained at any temperature thus.

Let η_t = viscosity of phenol at t°C.

Let d_t = density of phenol at t°C.

Let T = number of seconds taken for phenol to flow in the oil viscometers.

Then $\eta_t = K \times d_t \times T_t$

Where K = constant for the oil viscometer at t°C.

The value for K will slightly alter with temperature, and this is obtained from a curve connecting K and temperature for any desired reading found as above. It greatly facilitates calculation to use logarithmic values in expressing the constant on the curve since the viscosity is easier to find by using the logarithms of the obtained time of flow and density from the equation.

$$\eta_t = K_t \times \text{time of flow} \times \text{density F°C of oil}$$

or $\log. \eta_t = \log. K_t + \log. (\text{time of flow}) + \log. (\text{density F°C})$

Thus η_t (dynes per sq. cm.) can be obtained.

With lubricating oils it was found that very few had an appreciable viscosity beyond the 250°C region (except heavy cylinder oils) and in most cases the viscosity curve followed the order of the lubricating power.

RESULTS

Water at 15°C =.01134. Oil, dynamo, (H.V.) (S.G. = .905) also used as a light gas engine oil

Temp.	*Vis.*	*Temp.*	*Vis.*
75°C	.1017	163°C	.0105
111°C	.0332	207°C	.0050

Hence beyond 200°C the viscosity of this oil is negligible.

Crank Chamber Oil (Bayonne) Also used as a medium gas engine oil.

Temp.	*Vis.*	*Temp.*	*Vis.*
74°C	.1264	133°C	.0232
86°C	.0866	155°C	.0134
109°C	.0461	215°C	.0070
114°C	.0344		

This closely approaches the previous oil's viscosity as the high temperature region is reached.

Heavy gas engine oil. A blend, S. G. 900–5 at 60°F.

Temp.	*Vis.*	*Temp.*	*Vis.*
75°C	.1719	159°C	.0160
116°C	.0441	211°C	.0040[1]

This is a slightly better oil at high temperatures.

Cold test Motor Oil.

Temp.	*Vis.*	*Temp.*	*Vis.*
110°C	.1135	180°C	.0199
160°C	.0293	225°C	.0084

This has a viscosity above .005 up to the 250°C region.

Twentieth Century Cylinder oil. (a filtered cylinder oil)

Temp.	*Vis.*	*Temp.*	*Vis.*
110°C	.1419	198°C	.0173
149–150°C	.0495	(Decomposition slightly)	

This is similar to cold test oil at high temperatures.

"Standard" Cylinder Oil. American. (A blended Black oil)

Temp.	*Vis.*	*Temp.*	*Vis.*
110°C	.185	198°C	.0187
161°C	.0436	250°C	.006[2]

Elektrion Rape Oil.

Temp.	*Vis.*	*Temp.*	*Vis.*
131°C	.5404	[3]191°C	.1024
159°C	.2333	[3]213°C	.0620

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[1] Decomposition Region.

[2] By extrapolation.

[3] Liberation of gas.

Castor Oil (first pressings)		*Sperm Oil*	
Temp.	*Vis.*	*Temp.*	*Vis.*
108°C	.1168	15.5°C	.780
130°C	.0597	17°C	.742
[4]157–8°C	.0304	545°C	.159
[4]198–9°C	.0145	89°C	.0578
[5]240°C	.005[6]	111°C	.0357

Thickened Rape Oil		*"Monogram" Motor Oil*	
Temp.	*Vis.*	*Temp.*	*Vis.*
75°C	.847	75°C	.180
106°C	.274	103°C	.0637
136°C	.123	127°C	.0332
		160°C	.0165

Russian Engine Oil		*Galician Engine Oil*	
25°C	2.441	25°C	2.517
50°C	.459	50°C	.508
75°C	.145	75°C	.198
80°C	.122	100°C	.0638
100°C	.058	125°C	.0319
125°C	.0247		
150°C	.016		

Victory Engine Oil		*Loco. Cylinder Oil*	
76°C	.2594	80°C	.660
100°C	.0944	100°C	.279
120°C	.0504	150°C	.0574
142°C	.028	180°C	.0265

Heavy Marine Engine Oil		*Medium Spindle Oil*	
70°C	.230	64°C	.1098
100°C	.0780	100°C	.0348
140°C	.0246	150°C	.0123
150°C	.0196		

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[4] Decomposition. [5] About. [6] By extrapolation.

Texas Engine Oil		*Russian Rape Oil*	
70°C	.181	70°C	.146
110°C	.0454	100°C	.0673
150°C	.0175	130°C	.0324
		150°C	.0219

	Δt	Absolute Viscosity at 15.5°C	η x 1000	Secs. in a Redwood at 15.5°C
Arctic Sperm	.881	.616	616	210
Sperm oil (old sample)	.8866	.780	780	269.6
Linseed (Dutch)	.933	.7679	767.9	266
Hempseed	.931	.8385	838.5	284.5
Nigerseed	.925	.9729	972.9	326
Sunflower	.924	1.1084	1108.4	352.2
Poppy	.926	1.1102	1110.2	354.5
Bean	.924	1.1113	1111.3	358.
Ravison	.919	1.1305	1130.5	452.4
Arachis	.9165	1.1316	1131.6	464.2
Neatsfoot	.9164	1.1378	1137.8	——[1]
Pale Cotton	.925	1.139	1139	445.8
Refined Colza (old sample)	.919	1.1515	1151.5	511.4
Japanese Rape	.919	1.1568	1156.8	523.6
Pale Olein	.898	.6449	644.9	212.2
Perilla Oil	.931	.6728	672.8	256
	19°C	*19°C*		
Pale Liver oil	.9275	.8450	845.0	289
Pale Whale oil	.922	.9951	993.1	353.2
Mineral Sperm	.823	.08744	87.44	48
Half White Mineral	.8693	.4143	414.3	154.4

[1] Deposited Stearine.

It will be noticed that in the various groups of the animal and vegetable oils that the iodine value increases as the absolute viscosity of the oil diminishes, and in the case of the semi drying oils, except cottonseed, the absolute viscosities are very close. Ravison oil has a much less viscosity than rape oil, and it invariably has a higher iodine value. The extra high viscosities of cotton seed oil, nut oil and neatsfoot are due to the presence of a considerable quantity of solid glycerides. Rape oil owes its high viscosity to the presence of erucin of high molecular weight, (1052 against 884 for triolein). The subject is complicated in the case of oils and fats due to the presence of (a) mixed glycerides (b) solid glycerides in solution (c) extraneous matter such as unsaponifiable, dye, etc. Primarily oils have high viscosities compared with other chemical families because of their high molecular weights. Castor oil owes its high viscosity to the presence of hydroxy compounds and consequent association (cf. glycerin). "Blown oils" and polymerised oils owe their increased viscosity to a corresponding increase in the size of the molecule, coupled with hydroxyl formation to a greater or less extent. Tung oil, with a high iodine value, has a high viscosity.

Viscosity of lubricating oils both fatty and mineral, generally diminishes rapidly with rise of temperature. Here again, the more viscous the oil at ordinary temperatures, the greater usually is its temperature coefficient. Artificially thickened oils (e.g. solutions of soaps in oils) rapidly lose their viscosity at high temperatures, again due to their high temperature coefficient, a behaviour common to most viscous solutions. From the fact that, in oil blending, the results for viscosity never obey the law of mixture, shows that physical action and association of different molecules to form aggregates must take place, though the actual changes are by no means understood. Small quantities of less viscous oils invariably lower the viscosity of a more viscous oil by much more than the calculated amount, and this fact is borne out by every oil manufacturer's or blender's experience.

Unfortunately, with the ever varying sources of the same kind of oil, together with the greater or less amount of dissolved extraneous bodies present which are never completely removed in refining, it is almost impossible to place the subject of oil viscosities on the same plane as that of pure substances, but by determining average absolute viscosities for the same kind of oil through a range of temperature a good deal of valuable information as to the purity of a sample of oil should be derived. In the present state of our knowledge, determination of the actual constitutional effects on the viscosity is practically impossible.

THE VALUE OF VISCOSITY RESULTS

No viscosity instrument can possibly reproduce the actual conditions under which lubricating oils are employed, and results furnished by them are purely arbitrary, but by accurately standardising each type of instrument and comparing all results with one such type, it is possible to arrive at an approximate comparative measure of viscosity. Undoubtedly viscosity determinations throughout a range of temperature, preferably that to which the oil is likely to be subjected, serve as a valuable guide to the suitability of an oil for lubricating purposes, especially if the chemical actions likely to take place and the conditions of lubrication are approximately known. (With hydro-carbon oils unless the temperature gets too high from insufficient or over lubrication, chemical action is a minimum.)

The more viscous a lubricant and the stronger the adhesion between it and the bearings, the greater the pressure it will sustain, but excessive viscosity creates superfluous fluid friction. Hence ideal conditions are those where the viscosity of the lubricant is just sufficient to keep the moving surfaces apart under the maximum pressure to be exerted. In all cases the viscosity of the lubricant should be in direct proportion to the pressure likely to be sustained, such pressure being considered normal to the oil film for the below mentioned reasons. Consider the film of oil which must be sufficiently viscous to keep the metal surfaces apart at the working temperatures. The layer in the center of the film may be considered at rest, the remainder of the oil each side being subjected to a simultaneous strain. Should the lubricant have a very low viscosity the equilibrium of the film will be destroyed, the more so the greater the velocity of the lubricated parts, and the oil will run off the bearings with consequent damage to them. However, by using a suitable lubricant, i.e. one having an appreciable viscosity and preferably changing little through the range to which it is subjected, this difficulty is overcome, the bearings are kept apart and consequently friction is reduced to a minimum and lubrication takes place. The greater the pressure normal to the centre layer of the oil exerted by the lubricated parts, the greater the tendency of the oil to squeeze out so that the viscosity should be sufficient to prevent the rupture of the centre layer at the maximum pressure attained.

Now that absolute viscosity of lubricating oils can be accurately and easily obtained it should be no great effort to obtain oils with viscosities at the working temperatures proportional to the pressures likely to be attained and sufficient to ensure proper lubrication.

Redwood (J. S. C. I. 5. 1886, 21.) after discussing fluid friction and motion with the laws obeyed by such moving liquids and surfaces, quotes Professor Thurston as follows, "Fluid friction is the friction of adjacent bodies of fluid in relative motion and is due to the formation of small whirls or large eddies in the two adjacent fields, the production of which absorbs energy from the flowing mass (stream) resulting in a rise of temperature equivalent to the heat energy so destroyed. The resisting property which thus effects this conversion and which is the cause of fluid friction is called viscosity. In the case of very mobile liquids and gases the resistance is of kinetic character rather than one due to intramolecular action, but the flow of viscous liquids is evidently greatly influenced by their molecular constitution."

OTHER APPLICATIONS

It is obvious from what has gone before that the viscometric method can be applied with advantage to any case where the utility of a substance depends on the molecular size of its ultimate particles. In recent years for example, it has been used to test the nerve of rubber, and the comparative value of gum solutions. These are instances of the applicability of viscosity as the most suitable specific property. But the authors would go further and would claim for this method that being one of the most constitutive physical properties (i.e. being almost entirely dependent upon the arrangement of the atoms in the molecule) it is eminently useful as a means of characterisation and detection. To this end they are applying it to the study of varnishes, essential oils, turpentines, waxes, and a variety of commercial products.

"EIN BEITRAG ZU DER FRAGE DER BILDUNG DES ASPHALTS"

C. Engler

Welche Art der Genese des Erdöls und des Asphalts man auch annehmen mag, die Bildung aus organischen Resten oder aus Metallcarbiden, muss man sich in allen Fällen vergegenwärtigen, dass wir es in den verschiedensten Asphaltarten mit relativ sehr hochmolekularen Verbindungen zu thun haben, die aus den hypothetischen Ausgangsmaterialien—seien dies nun die aus Fett-, Wachs-, Harz-, etc. Resten oder die aus Acetylen und Wasserstoff gebildeten Kohlenwasserstoffe nur durch einen Polymerisations vorgang gebildet haben können.

Polymerisationsvorgänge spielen in der Natur bei der Bildung sehr vieler Verbindungen der organischen Stoffwelt eine wichtige Rolle. Schon die erste Bildung primärer Kohlenhydrate erfolgt aus der Kohlensäure der Luft über den Formaldehyd durch eine Polymerisation worauf namentlich auch die neuesten Versuche von *Curtius* u. *Franzen* hinweisen. Das Stärkmehl, die Cellulose, die Eiweissstoffe, auch die Harze, die neugebildeten und die fossilen, sind Polymerisationsprodukte; Graphit und Diamant dürften ebenfalls als Polymere des gewöhnlichen Kohlenstoffs angesehen werden. Und neuerdings bemächtigt sich auch die Technik dieses Prozesses: Oele werden zu Lark, das Condensat von Phenolen mit Formaldehyd zu Backelit, Isopren zu Kautschuk polymerisiert.

Die namhaftesten Forscher auf dem Gebiete der Asphaltbildung wie *Peckham, Richardson, Zaloziecki, H. Köhler, Graefe* u. a. bekennen sich zu der Annahme, dass die Asphalte Polymerisationsprodukte sind. Im Grunde genommen differieren ihre Ansichten abgesehen von der Frage des Urmaterials, nur in der Frage nach der Ursache der Polymerisation.

Manche weisen dabei dem Schwefel eine Hauptrolle zu, Andere dem Sauerstoff, wieder Andere aber halten die Annahme einer Mitwirkung irgend welcher Katalysatoren oder dritten Stoffe für unnötig, indem sie die Asphalte nach ihrer elementaren Zusammensetzung lediglich als die natürlichen Abbau—oder Umsetzungsprodukte der Ausgangsmaterialien ansehen.

Wenn ich auch eine Mitwirkung des Schwefels in vielen Fällen nicht in Abrede stelle, so kann ich demselben für die Asphaltbildung ganz im Allgemeinen nicht eine generell ausschlaggebende Rolle beimessen, halte vielmehr die Mitwirkung des Sauerstoffs dabei für das wichtigere. Dafür sprechen nicht blos Zusammensetzung und chemische Beschaffenheit des Asphalts, sondern auch geologische Gründe, so vor Allem das Fehlen von Asphaltlagern in grossen Tiefen und die Beschränkung seines Vorkommens auf den oberen, dem atmosphärischen Sauerstoff zugänglicheren Schichten. Dabei dürfen wir aber die Asphalte nicht lediglich als Oxydationsprodukte von fertigen Erdölkohlenwasserstoffen ansehen, müssen vielmehr auch mit einer direkten Bildung derselben aus gewissen Uebergangsstoffen des organischen Ausgangsmaterials in Petroleum rechnen, wie ich solches in meinem Systeme der Bitumenbildung [1] schon ausführlich auseinandergesetzt habe.

Ich vertrat, nachdem gelegentlich einer von *Kronstein* in meinem Laboratorium ausgeführten Arbeit schon 1902 darauf aufmerksam gemacht worden war, stets die Ansicht,[2] dass Autoxydation und Polymerisation in engem Zusammenhang stehen und dass die letztere durch erstere in beschleunigendem Sinne beeinflusst werde.

Exakte Versuche über die Beschleunigung der Polymerisation von Kohlenwasserstoffen durch gleichzeitige oxydierende Wirkung von Sauerstoff lagen bisher nicht vor, wenngleich nach bisherigen Wahrnehmungen ganz kleine Mengen gleichzeitig einwirkenden Luftsauerstoffs eine solche Beschleunigung zur Folge hatten. Es sind nun aber neuerdings im Karlsruher chemischen Laboratorium von Standinger und Lautenschläger umfangreiche Versuche über diese Frage angestellt worden, deren Ergebnisse ich hier mitteilen kann. Sie bestätigen durchweg die Richtigkeit meiner bisherigen Annahme.

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[1] Chem. Ztg. 1912, S. 65 u. *Engler-Höfer* "Das Erdöl" Bd. I, S. 35.

[2] *Engler* u. *Weissberg* "Kritische Studien über die Vorgänge der Autoxydation" Braunschweig 1904, S. 179 *Engler* "Die neueren Ansichten über die Entstehung des Erdöls," Berlin 1907, S. 25; Zeitschr. f. angew. Chem. **21** (1908), S. 1585. U. S. W.

Ganz allgemein möge noch auf Folgendes hingewiesen werden. Der Polymerisation unterliegen hauptsächlich ungesättigte Verbindungen, doch können auch gesättigte Verbindungen dadurch polymere Produkte liefern, dass, wie z. B. bei gesättigten Kohlenwasserst offen durch Oxydation oder Wirkung des Schwefels (*Cl. Richardson*), ungesättigte Reste entstehen. Je nach der chemischen Natur der ungesättigten Gruppe verläuft die Polymerisation mit sehr verschiedener Geschwindigkeit. Manche verlaufen spontan, manchmal sogar explosionsartig, andere langsam und wieder andere bedürfen der Katalysatoren um deutlich sichtbare Polymerisation zu erzielen. Sehr oft durch diese, namentlich aber durch Wärme wird im Allgemeinen der Vorgang beschleunigt. Ob auch durch Druck, soll womöglich durch in meinem Laboratorium zur Zeit im Gang befindliche Versuche entschieden werden.

Endlich sei auch noch an den sehr interessanten Befund Stobbe's erinnert, wonach durch Animpfen mit einer kleinen Menge schon polymerisierter Substanz und damit der Schaffung eines Polymerisationskernes der Vorgang ganz wesentlich beschleunigt wird.

Bei der folgenden Untersuchung wurden in zwei Parallelversuchen je 10 g Substanz in kleinen Kölbchen mit Kohlensäure und mit Sauerstoffgas im Thermostaten auf 80° bestimmte Zeiten erwaermt. Nach Beendigung der Erwärmung und nach Abdisillieren des nicht polymerisierten Teile wurden die rückständigen Polymerisationsprodukte gewogen. In der folgenden Tabelle sind die mit einer Anzahl von Kohlenwasserstoffen erhaltenen Resultate vergleichsweise nebeneinander gestellt:

Kohlenwasserstoffe	Prozentgehalt der veränderten Stoffe nach der Polymerisation							
	in Kohlensäure				in Sauerstoff			
	nach 1	2	3	4 Tg	nach 1	2	3	4 Tg
Limonen..........	2	4	5	6	4	6	8	9
Phellandren.......	4	6	8	9	9	13	16	21
Pinen.............	1	2	2	3	3	4	4	5
Myrcen...........	8	13	18	22	20	30	40	50
Camphen.........	3	4	5	6	5	7	8	9
Jsopren...........	5	6	7	8	10	14	18	23
Dimethylbutadien..	12	16	18	22	18	24	26	28
Tetrahydrobenzol ..	0,8	1	1,3	1,5	3	4	5	7
Cyclopentadien —..	nach 2		6	Std.	nach	2		6 Std.
	45		68			75		94
Styrol—..........	nach 10		20	Std.	nach	10		20 Std.
	14		22			35		67

Die erzielten Resultate lassen die beschleunigende Wirkung des Sauerstoffs bezw. der Autoxydation durchweg erkennen. Noch viel in die Augen springender fallen die Versuche aus, wenn man die Polymerisation im Autoklaven bei Gegenwart von Kohlensäure und von Sauerstoff miteinander vergleicht. Während z. B. Pinen in Kohlensäure-Atmosphäre dabei sich nur wenig verdickt, wird es in Berührung mit Sauerstoffgas zu einem dicken kaum fliessenden Syrup.

Unter der Annahme, dass kleine Mengen der bei der Autoxydation ungesättigter Kohlenwasserstoffe entstehenden Peroxyde den katalytischen Anstoss geben könnten, wurden auch vergleichende Versuche durch Zusatz vorher bereiteter Peroxyde ausgeführt. Es zeigte sich wohl Beschleunigung, doch nicht in gleichem Grad, wie mit freiem Sauerstoff. Jedenfalls zeigen aber die Versuche, dass schon ganz geringe Mengen Sauerstoffes ausreichen die Polymerisation ganz erheblich zu beschleunigen. Jedenfalls sind die aufgenomenen Sauerstoffmengen so gering, dass ein eventueller Einwand, die Verdickung der oele sei eine

Folge gebildeter Oxydationsprodukte, hinfällig wird. Diese Versuche bilden eine weitere experimentelle Stütze für die Richtigkeit der Annahme, dass der Sauerstoff der Luft bei dem Polymerisationsvorgang der Bildung des Asphalts eine Rolle spielt.

Durch Versuche von *Ubbelohde* u. *Schapringer.* welche unabhängig von vorstehenden Untersuchungen im Chemischtechnischen Institut zu Karlsruhe ausgeführt wurden und deren Resultate bereits in gedruckter Dissertation vorliegen,[1] wird festgestellt, dass auch bei der Polymerisation von Holzöl die Anwesenheit von Luftsauerstoff beschleunigend wirkt, was an der Zunahme des spez. Gewichts und der Abnahme der Jodzahl, sowie des Lichtbrechungsvermögens einwandfrei verfolgt werden konnte.

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[1] *Schapringer,* Dissertation Karlsruhe, 1912.

(*Abstract*)

A REMARKABLE CARBONACEOUS CLAY DEPOSIT NEAR PUTNAM, NEW MEXICO

William Foster
Princeton, N. J.

A remarkable caramel-like deposit has been discovered near Putnam, New Mexico. The deposit appears to be extensive, and when the material, which is everywhere covered with sand, is dug it is of the consistency of gelatin. On burning in an open vessel, the ash amounts to more than 50 per cent, and it is primarily clay. Excluding mineral matter, the composition corresponds closely to that of peat. The gases obtained by destructive distillation were principally hydrogen, the oxides of carbon, and methane. The material is sparingly soluble in organic solvents, but forms a collodial solution with water, and exhibits Brownian movements. It is readily precipitated by the addition of electrolytes. The material does not respond to the α-naphthol test for carbohydrades. While in its chemical domposition it most resembles peat (excluding mineral matter), it has been suggested that it is most like cannel coal as to the manner in which it may have been formed. The deposit appears to be a carbonaceous clay in a very fine state of division.

(*Abstract*)

CRUDE OIL GAS PRODUCERS OF THE PACIFIC COAST

HARRY A. GRINE
Los Angeles, Cal.

In my paper on "Crude Oil Gas Producers of the Pacific Coast" I have attempted to give some idea of the nature of the oil gas producer development and a brief description of several representative types.

The development of the oil gas producer on the Pacific Coast has made little progress until the past five years and has been almost wholly of a practical and non technical nature.

Oil vaporizers, of which there have been many developed, are distinctly different from the oil gas producer. The former makes an unstable vapor gas by utilizing the heat of the engine exhaust to heat the oil; the latter makes a stable or fixed gas by dissociation and recombination of the elements of the oil by partial combustion. The oil vaporizer is simply a magnified carburettor.

Oil gas producers of the Pacific Coast which have been commercialized are conveniently divided into several types according to the methods of introducing the oil and the methods of causing the combustion of the oil as follows:

Type A—Non-Atomizing and Flame Gasification.

Type B—Atomizing and Flame Gasification.

Type C—Atomizing and Non-Flaming, or uniform Combustion and Completion of Gasification in a Solid Carbon Fuel Bed.

The various methods of introducing the oil and burning it together with the temperatures secured by these different methods are the controlling factors which determine the nature of the gas and the amount of carbondust or tar by-product formed.

Representative gas analyses of gas made in the different types show variations principally in the percentages of Olefine Hydrocarbons, Carbon Monoxide and Hydrogen.

The following analyses are representative of the different types.

	% by volume		
	Type A	Type B	Type C
Carbon Dioxide	4.5	5.0	6.2
Oxygen	[1]	0.5	0.3
Olefine Hydrocarbons	4.8	3.0	1.0
Carbon Monoxide	7.8	11.8	15.1
Methane	8.7	9.6	4.6
Hydrogen	9.0	6.0	5.4
Nitrogen	65.2	64.1	67.4
	100.0	100.0	100.0

[1]Undetermined.

Nitrogen by difference.

The early supposition that the formation of large quantities of carbon dust was unavoidable in the partial combustion of crude oil to form producer gas has been proven erroneous by later development.

Prevention of the formation of this product by proper control of the gasifying conditions has proven much more successful than mechanical devises for extracting the carbon dust and tar.

The commercial crude gas producer must satisfy the following conditions where the gas is intended for use in gas engines.

1. There must be a minimum production of solid carbon dust or tar.
2. The supply of gas must be under complete control for variable loads.
3. The gas must be uniform in quality.
4. The generator should be continuous in its operation.

In order to allow ample time for the decomposition and recombination of the elements of the oil the producer should be of sufficient size to give a slow velocity of gas travel. This has been largely overlooked in most of the generators.

The carbon dust formation may be under almost complete control by a proper control of temperature. Attempts to force a large production of gas in small generators by using high temperature flame combustion have resulted in excessive carbon dust formation.

Much improvement may be looked for in the crude oil gas producer when a proper technical study of the causes which produce favorable or unfavorable results is made. They can only be determined by a close analytical study of the pressures, temperatures and volume and composition of gas produced per unit volume of gasifying chamber.

(*Abstract*)

AN APPARATUS AND METHOD FOR DETERMINING HYDROGEN SULPHIDE IN ILLUMINATING GAS

E. P. Harding and Einer Johnson
University of Minnesota, Minneapolis, Minn.

The principle of this method is the absorption of hydrogen sulphide by a solution of cadmium chloride, its liberation in a partial vacuum by means of hydrochloric acid and its titration with a standard iodine solution.

Comparative tests with this method and the gravimetric cadmium chloride and the Tutwiler methods gave the following results:

Coal Gas

Grav. $CdCl_2$	Vol. $CdCl_2$	Tut.
2.72	2.93	31
0.53	0.46	22
0.89	0.79	27
1.58	1.54	38
1.00	0.92	24
2.68	2.65	30
1.31	1.25	23
2.35	2.26	29
1.81	1.72	27
0.88	0.84	18
4.86	4.76	110
2.73	2.69	65
1.22	1.18	25
2.72	2.61	28
1.65	1.59	30
1.30	1.26	26
1.09	1.04	24

Water Gas

Grav. $CdCl_2$	Vol. $CdCl_2$	Tut.
0.59	0.55	16
0.26	0.23	8
0.40	0.36	11
0.15	0.13	5
0.34	0.31	12
Crude Coal Gas		
225	220	360
190	188	310

Advantages of this Method.—The principal advantage of Tutwiler's method is its rapidity. A test can be made in about three minutes. Its chief disadvantage is its inaccuracy. The results obtained are only approximate especially on the partially purified gas, the error varying from 1000 to 4000 per cent as shown by the comparative tests above. This error is due to the titration of the gas with the iodine solution, the unsaturated hydrocarbons, cyclopentadiene[1] and probably sulphur compounds other than hydrogen sulphide reacting with the iodine. Results on the crude gas are less inaccurate, the error amounting to about 15 per cent. This is of course due to the much greater ratio between the amount of hydrogen sulphide present and the other compounds with which the iodine reacts. McMillar states in the original publication of Tutwiler's method that 15 grains of hydrogen sulphide per 100 cu. ft. of gas could escape detection. In the writer's experiments, in no case did the Tutwiler show less than 10 grains per 100 cu. ft. on clean coal gas nor less than 4 grains per 100 cu. ft. on clean water gas.

The gravimetric cadmium chloride method is the most accurate in use at the present time. The great objection to this method, however, in control work is the length of time required to make a determination. The purifying boxes foul quite rapidly and in determining their efficiency, tests should be made rapidly and as nearly simultaneously at inlet and outlet of purifier as possible. A method which requires hours for a test becomes impracticable. The large bulk of cadmium chloride solution used allows absorption of other sulphur compounds than hydrogen sulphide, which when oxydized with the bromine give too high results. Another objection is the large amount of cadmium sulphide precipitate required to produce an amount of barium sulphate which can be readily and accurately weighed. When a sample of 0.1 cu. ft. of gas is taken, each milligram of $BaSO_4$ is equivalent to 2.252 grains of sulphur per 100 cu. ft. Thus for partially purified gas containing but a fraction of one grain of hydrogen sulphide per 100 cu. ft., a number of cu. ft. of gas must be used in order to obtain a weighable precipitate.

The volumetric cadmium chloride method has several advantages over the gravimetric method. Accurate results are obtained on a much smaller volume of gas; a smaller volume of cadmium chloride solution causes less absorption of sulphur compounds other than hydrogen sulphide; the method is much more rapid, requiring for a determination instead of hours, from seven to ten minutes depending upon the purity of the gas.

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[1] London Journal of Gas Lighting, April 5, 1910, p. 41; April 12, 1910, p. 18.

The advantages of the volumetric cadmium chloride method over the Tutwiler are several. Twenty-eight times as much gas is used in the average determination as is used in the Tutwiler; the burette readings are one-tenth those of the Tutwiler and much more accurate results on gas of low hydrogen sulphide content are obtained. A test can be made in from seven to ten minutes.

DIE ZÄHIGKEITSBESTIMMUNG VON FLUESSIGEN SCHMIERMITTELN

PROF. DR. HOLDE
Berlin-Lichterfelde

Seit nahezu 3 Jahrzehnten ist man gewöhnt, die Zähigkeit von Schmierölen im Handelsverkehr, in der Technik und in derjenigen Literatur, welche auf die Bedürfnisse und den Gebrauch in der Technik Rücksicht zu nehmen hat, in seg. ENGLERzahlen, (Deutschland, Oesterreich, Ungarn, Russland, Rumänien) SAYBOLTzahlen (Standard Oil Co., Vacuum Oil Co.) REDWOODgraden, (England) u.s.w. auszudrücken, die weder untereinander noch zu der wirklichen specifischen Zähigkeit eine ohne weiteres erkennbare Beziehung haben. Die auf grundsätzlich verschieden konstruirten Apparaten erhaltenen Zahlen geben vielmehr nur an, in welchem Verhältniss die Ausflusszeiten der zu prüfenden Flüssigkeit zu derjenigen von destillirtem Wasser oder von Rüböl auf den genannten Apparaten von bestimmter Temperatur stehen, sodass in den verschiedenen Staaten weder für die Zähigkeit ein gleicher noch ein auch nur annähernd der wirklichen specifischen Zähigkeit entsprechenden Ausdruck zur Kennzeichnung dieser wichtigsten Eigenschaft flüssiger Schmiermittel benutzt wird. Beim Englerschen variirt der Quotient zwischen dem sog. Englergrad und der wirklichen specifischen Zähigkeit zwischen 3,6 und 4,10, im Mittel ist also die wirkliche specifische Zähigkeit bezogen auf Wasser von 0°—1 etwa 4 mal so gross als sie auf dem Engler-Apparat gefunden wird, die entsprechenden Quotienten auf den Apparaten Englands und Amerika differiren wiederum erheblich von jenen sogenannten Quotienten und untereinander, womit also, was dem Fachmann natürlich nicht neu ist, erwiesen ist, dass die verschiedenen Staaten hier eine ziemlich willkürliche von einander ausserdem ganz verschiedene und scheinbar durch Gewohnheitsbedürfnisse zu sehr beeinflusste ausdrucksweise für die Zähigkeit der Oele benutzen.

Es liegt nun in meiner Absicht, in der vorliegenden Mitteilung an der Hand einiger Versuche anzuregen, die wirkliche specifische Zähigkeit der Oele mehr in den Vordergrund bei allen Erörterungen in der Literatur, auch im Handelsgebrauch u.s.w. zu rücken, als dies bisher geschehen ist.

Um die Sachlage genau zu erkennen, bedenke man, was es bedeutete, wollte man z. B. die specifischen Gewichte der Oele statt zu ihren wirklichen Beträgen zum 4ten Teil dieser Beträge in einem Land, im anderen Land zum 8ten Teil dieser Beträge angeben u.s.w. Man vergegenwärtige sich aber auch, um objektiv vorzugehen, welche Umstände dazu geführt haben, zur Zeit, als die technische Schmiermittelprüfung begann, in Deutschland für tarifarische Zwecke etwa vor 30 Jahren, nicht gleicht entsprechend der specifischen Gewichtsbestimmung die specifische Zähigkeit der Oele direkt zu bestimmen, sondern ein willkürliches Maass z.B. in Deutschland den Englergrad, als Maass der Zähigkeit einzuführen.

Der Grund liegt darin, dass die mit der Schaffung von Normalapparaten betrauten Stellen, insbesondere auch der Erfinder des Engler-Apparats Excellenz Engler sich zunächst mit Recht sagten, dass für die mit der technischen Schmierölprüfung für tarifarische Zwecke u. dergl. zu betrauenden jüngeren Beamten, die oft nicht mit grosser naturwissenschaftlicher und apparativer Vorkenntniss ausgestattet sind, die unmittelbare Bestimmung der wirklichen specifischen Zähigkeit auf den in Frage kommenden difficilen Glasapparaten aus praktischen Gründen nicht in Frage kommen könne.

Die specifische Gewichtsbestimmung ist hingegen genau bis auf die 4te Decimale mit den einfachsten Apparaten auszuführen.

Deshalb hat man wie in Deutschland so auch anderweitig einfachere Apparate ersonnen, auf denen auch ein weniger wissenschaftlich gebildeter Beamter, ja jeder einigermassen geschickte Laborant, einfache Bestimmungen der Ausflusszeit von Oelen ausführen und sie in Vergleich zur Ausflusszeit von Wasser als Englergrad, Redwoodzahl u.s.w. setzen kann.

Man ist sich aber damals noch nicht bewusst gewesen, dass man auf diesen Apparaten nicht nur die Ausflusszeiten und durch deren Vergleich mit Wasser ein ganz rohen Vergleich der Zähigkeit ermitteln kann, sondern dass man auch auf diesen Apparaten tatsächlich durch Anwendung einer Umrechnungsformel, die erst etwa 20 Jahre von Ubbelohde aufgefunden wurde, die wirkliche specifische Zähigkeit der Oele leicht ermitteln kann.

Diese Umrechnungsformeln stellte Ubbelohde fest, als er Tabellen für unmittelbare Berechnung der Englergrade aus den ermittelten Ausflusszeiten von 50,100 und 200 Oel aufstellte und hierbei gleichzeitig rechnerische Beziehungen zwischen der Zähigkeit nach Engler und der wahren specifischen Zähigkeit geben wollte. Er schlug hierbei zunächst vor, da zur Ermittlung der wahren specifischen Zähigkeit aus den Englergraden noch die Bestimmung des specifischen Gewichts hinzuzuziehen war, unter Umgehung dieser letzteren Bestimmung, um einen der wahren specifischen Zähigkeit angenäherten Wert, nämlich den sog. Zähigkeitsfaktor zu ermitteln.

Diesen Vermittlungsvorschlag möchte ich, so sehr ich wie jeder Fachmann die hier in Betracht kommenden grundlegenden Arbeiten Ubbelohdes hochschätze, nicht gern acceptiren, da er mir als ein durch praktische Erwägung nicht ausreichender gestützter Grund erscheint, nicht die volle Konsequenz aus den Ubbelohdeschen Arbeiten zu ziehen und durch die einfache Mitberücksichtung des specifischen Gewichts die wirkliche specifische Zähigkeit nach Engler zu bestimmen und ein ähnliches Vorgehen auch für die Apparate anderer Länder zu planen. Wenn Herr Ubbelohde selbst aus Gründen einer gewissen Zurückhaltung gegenüber bestehenden Gebräuchen diese Konsequenz noch nicht zur praktischen Forderung erhoben hat, so glaube ich nach Unterredungen, die ich über diesen Punkt mehrfach mit ihm gehabt habe, sein Einverständniss dafür zu besitzen, dass das hier bezeichnete Ziel nunmehr, wo wir beim Engler-Apparat über feste Normen in den Abmessungen und in der Versuchausführung verfügen, und ähnliche Bestrebung für die Apparate der anderen Länder teilweise verwirklicht oder in der Verwirklichung begriffen sind, etwas bestimmter verfolgen können. Dies wird eine erwünschte internationale Verständigung wenigstens auf einem wichtigen Teilgebiet bedeuten.

In der nachfolgenden Tabelle will ich Ihnen nun an einer Reihe von Versuchen und Berechnungen des Zähigkeitsfaktors und der specifischen Zähigkeit aus den Zähigkeitsbestimmungen nach Engler und aus der direkten Zähigkeitsbestimmung auf dem vorzüglichen von Ubbelohde verbesserten F. TRAUBEschen CAPILLARzähigkeitsmesser genau zeigen, welche Fehler man begeht, wenn man die specifische Zähigkeit oder den Zähigkeitstfaktor aus den Englergraden unter Benutzung der Ubbelohdeschen Umrechnungsformel bestimmt.

Sie ersehen, dass die der auf dem Traubeschen Capillarviscorimeter bestimmten specifischen Zähigkeiten gegenüber den durch Umrechnung aus den Englerzahlen ermittelten specifischen Zähigkeiten bei Oelen Englergrad, 6–9, 541 bei 20° nur + 3 bis + 5% mehr betragen, sodass wir unter Anbringung einer mittleren Korrektur von etwa, 4,2% die wirklichen specifischen Zähigkeiten mit einer annähernden Genauigkeit von etwa 1% aus den Englergraden berechnen können. Nur bei dem sehr dünnflüssigen Oel 1 (Englergrad 5,0 bis 10°) würde der Fehler fast + 4% betragen. Dies würde aber praktisch da der absolute Betrag der Zähigkeit gering ist, wenig belangreich sein.

Sie sehen gleichzeitig, dass die Zähigkeitsfaktoren um 2,4 bis fast 100 Einheiten mit wachsender Zähigkeit der Oele höher sind als die specifischen Zähigkeiten,

Es liegt also kein Grund vor, diese Zahlen, die absolut genommen erheblich wechselnde Abweichungen gegenüber den specifischen Zähigkeiten zeigen, einzuführen, und auch Ubbelohde scheint den letzteren Zahlen in seinem neuesten Vortrag über die Theorie der Reibung, den er im April d.J. in München gehalten hat, den Vorzug gegeben zu haben.

TABELLE

Beziehungen zwischen Englergrad, specifische Zähigkeit und Zähigkeitsfaktor

Oel No.	Englergrad bei 20°	Spec. Zähigkeit (Wasser 6°−1)		Differenz b^{I-II} % vm II	Quotient $\frac{b^{II}}{a}$	Zähigkeitsfaktor
		bestimmt aus F. Traube's Capillarviskorimeter	berechnet aus dem Englergrad			
1	5,03	18,8	17,4	+8	3,74	19,8
2	6,90 (100°)	24,6	23,4	+5,1	3,57	27,6
3	10,0	37,7	36,6	+3	3,77	40,4
4	43,1	165	159	+3,8	3,82	175,4
5	615	2525	2409	+4,8	4,10	2504
6	541	2212	2120	+4,3	4,09	2203

(*Abstract*)

THE EFFECT OF EXPOSURE ON BITUMENS

Prévost Hubbard and C. S. Reeve

This paper describes investigations conducted for a year on eight typical samples of bituminous road materials which were subjected to exposure tests for periods of one, two, four, six, eight and twelve months. Changes in weight, consistency and insoluble organic matter were determined at the end of each period.

All of the materials showed an increase in hardness due to exposure and an increase in insoluble organic material. Tar products lost weight continuously throughout a period of twelve months, while the petroleum and asphalt products showed either an increase in weight or only a comparatively slight loss. An increase in insoluble organic matter was noted which was considerably in excess over that calculated from the percentage loss in weight of the samples. This increase accompanies the hardening of the materials.

It is concluded that the hardening of all bitumens upon exposure is not due to loss of the lighter constituents by volatilization alone, but also to oxidation and reactions occurring between certain constituents of the bitumens. Such reactions would seem to account for the increase in insoluble organic matter. The increase in insoluble organic matter in tars demonstrates that so-called free carbon is actually formed in tars upon exposure.

THE USE OF NATURAL GAS IN THE MANUFACTURE OF OPEN HEARTH STEEL

Norwood Johnson
Pittsburgh, Pa.

The first use of Natural Gas in the manufacture of open hearth steel was at the Homestead Steel Works of the Carnegie Steel Company on October 27th 1886, and it is still used for that purpose in all of the open hearth departments, in the above works to the present time, where they now have 64 Open Hearth furnaces. It is also used by the United States Steel Corporation in all of its open hearth departments, wherever obtainable for the reason that, as a fuel for this purpose, it has no equal. It was at once recognized as an ideal fuel for metallurgical purposes for the following reasons:—

1st. Having a high heat value.
2nd. Not loaded with useless nitrogen.
3rd. Easily handled.
4th. Much easier to keep clean than with a producer gas.
5th. Generally much cheaper.
6th. Gives a larger output than any other fuel.

It will never be fully appreciated by those now using it until they are compelled to use other fuel; requiring about 5,000 cu. ft. of natural gas, at eight ounce pressure, to melt one ton of open hearth steel. These figures represent the best results obtainable in the latest improved furnaces.

The general analysis of this gas may be reported as follows:—

Carbon Monoxide, Co	1.8%
Methane, or Marsh Gas, CH_4	94.5%
Ethylene, sometimes called Illuminants C_2H_4	1.2%
Nitrogen, N	2.5%
	100.0%

The average amount of moisture in a cu. ft. of gas is .56 grains. It is 58% as heavy as air, and the average calorific value is high calorific 1045 B.T.U.........lower calorific value 970 B.T.U.

COMMERCIAL ASPECTS OF THE COAL BRIQUETTING INDUSTRY

CHARLES T. MALCOLMSON
Chicago, Ill.

Next to agriculture, the production of coal is the most important factor in our national wealth. This country now leads the world with a coal production of over one-half billion tons. As in all new countries, the national resources are exploited by private individuals for immediate returns and large profits, with studied disregard of economy or future requirements. This depletion is of serious consequence when it extends to coal, which cannot reproduce itself. We are told by experts, that at our present rate of consumption, our coal will last about two hundred years.

Recently the conservation of our natural resources has become an active movement, particularly with reference to necessities which affect the people directly, or are a controlling factor in the cost of living. There is no industry however large, nor wage earner however small, that is not affected more or less directly by the cost of coal. The present condition of the bituminous coal industry, which forces fuel on the market at ridiculously low prices, is too demoralizing to be maintained much longer. With the inevitable reaction must come a solution of the difficulty, which will place this important industry on a sound business basis.

In digging coal only fifty to sixty per cent is actually brought to the surface; the balance, in the form of pillars, top or bottom coal, fine coal, dust and thin veins, is left and can never be recovered. At the prices paid today for bituminous coal, the operator must steal from tomorrow in order to make a showing for today. Overproduction is the cause, and cut-throat competition the result. New mines with improved methods of mining are constantly being opened up, so that the old mines must either be shut down, or more ruthless methods and criminal wastefulness resorted to, in order to meet competition.

The high quality of our coal, the comparatively easy mining conditions and the fact that we have not been subjected to foreign competition, have thus far postponed the settlement of this issue. Similar conditions existed in Germany prior to 1895. At that time the German Coal Cartel or Rhenish Westphalian Coal Syndicate was formed, which was the greatest combination of its kind in the world, with an annual output of 50,000,000 tons. This is the organization which has enabled Germany to develop her coal exports in the face of the enormous competitive power of England, favored as the latter is by a larger production of high grade coal and the greatest shipping service in the world. The leading ideas of the German compact are to abolish price competition and regulate production. There are many degrees of development in these pools, from mere agreements on prices, terms of sale, restrictions of production, divisions of territory, etc., to highly organized aggregations of capital in which individual members give up a large part of their independence and agree to act under a central authority with extensive powers.

The existing laws of our country governing Trusts will not permit agreements for the regulation of prices and production, and refinements in methods of mining and preparing coal to increase the total revenue, must be substituted.

Payment of miners on the "mine-run basis,"and "shooting from the solid" have resulted in an increased degradation of the coal, with consequent lower revenue to the operator. Competition has forced cleaner preparation and a greater number of sizes, until today we have eighteen sizes marketed in Illinois, when only three are really required. The overproduction of fine coal has developed the mechanical stoker in large manufacturing centers, so that there is a shortage of fine coal during the spring and summer months; when the price of fine coal or screenings reaches the cost of producing mine-run, lump coal is often crushed at the mine to meet the requirements. This demand for fine coal has given a false impetus to the operator, so that during the winter months when there is an increased demand for sized coal, the overproduction of fine coal causes a slump in the market, and a reduction in the total revenue of the mine. Seventy-five per cent of the coal produced is consumed by steam plants, coke ovens, and other industrial concerns, in which the demand for fuel is practically constant throughout the year. Such fluctuation in demand as the records show is due to the difference between the summer and winter requirements of the domestic trade. This difference as applied to the total monthly production is obviously small, as shown by the Government and State reports. These statements apply more generally to bituminous coal, which represents approximately 85 per cent of our total coal production.

When a market is so sensitive to conditions of supply and demand the reasons are not hard to find. Undoubtedly the main reason is that the coal will not stand storage without loss. The truth of this statement is illustrated by the steady anthracite market; the price, however, is systematically regulated with a view to stimulating the movement of coal during the summer months, as anthracite is primarily a domestic fuel.

None of our bituminous coal can be stored without depreciating its fuel value. This is especially true of the finest of high grade coal and of all kinds of low grade coal; which brings us to the main subject of this paper,—briquetted coal.

Coal briquetting originated on the European Continent; the first commercial machine having been built in France in 1842. But Germany has far outstripped other countries in the development of the art, supplying in 1909 over 73%[1] of the world's production of coal and lignite briquets. It is said[2] that the briquetting industry was stimulated in Germany by local necessity, the native coals being scarce and inferior; and also by exploitation on the part of the Coal Cartel.

The report[3] to which we have already referred, deals further with facts which bear directly on conditions in America. It states that the briquet industry in Great Britain is confined principally to South Wales, where the plants are operated in connection with the collieries. The excellence of the low volatile Welsh coal has been a factor in establishing these briquets, which

[1] (Robert Schorr.)

[2] Report of Royal Commission Gt. Britain.

are low in ash and require a small amount of binder. The industry has suffered in England because, for the most part, the plants are operated independent of collieries; insufficient care has been taken in selecting the raw materials; no washed slack is used; eggettes are manufactured which are expensive owing to large percentage of pitch required and breakage in manufacture. Briquet factories have not flourished in the northeast of England for the following reasons:

"1. Facilities for shipping small coal to the Continent where briquets are made on scientific lines.

"2. Large use of coal for coking.

"3. Good market for fine coal in industrial plants.

"4. Comparatively low price of screened lump coal at northeast ports, with which briquets must compete."[3]

The demand in the United States has been towards briquets, of such size and shape as would replace the commercial sizes of prepared bituminous and anthracite coal. The very low price obtained for coal has left small margin for the briquetting charge. The binder represents more than half this charge, so that every effort must be made to keep the percentage of binder down, and at the same time produce merchantable briquets. Presses of large output decrease the manufacturing cost on such items as labor, fuel and fixed charges, without reducing the binder cost. the result of these conditions has been to develop briquetting presses of the plunger type, having a large output of small briquets.

European experience has taught us that in order to establish an economical and therefore merchantable product, briquets must be made in a form adapted to the use for which they are sold. The large rectilinear briquets exported by British concerns do not meet the demands of American practice, as they require too much labor in handling, and must be broken up before being used. On account of their high binder content, eggettes or boulets are not satisfactory except when made from anthracite coal, and then only when the greatest care is taken in their manufacture. The manufacturing cost of these briquets is such that they can compete only with anthracite stove sizes for domestic

[3] Report Royal Commission Great Britain.

use, which is the most critical trade to satisfy. Hence an excess of pitch binder is often fatal to the business, giving a setback to the industry in general. The attempt is frequently made to utilize the waste anthracite coal known as "culm," which is the dust passing through 3-32″ round hole screen. This culm contains from 15 to 35% ash, and tends to make a slow burning and smoky fuel of lower calorific value than the prepared sizes of anthracite. The culm is so fine that reduction in ash by washing is very difficult; and the separation of impurities from the coal by dry processes has yet to be perfected.

Two distinct classes of briquetting machines have been developed in Europe, known as the plunger and rotary or Belgian type. Briquets made on the plunger type of presses vary from 2 to 22 lbs. in weight, and are usually rectilinear. The output is small, owing to the mechanical difficulty in moving the heavy reciprocating parts. Plunger presses have the advantage of making a uniform product in which a small binder content is permissible on account of the high pressure obtainable. There is very little waste in operating these machines. The rotary or roll presses have relatively a larger output than plunger presses, if we consider the size of the briquets. The necessity of more binder, owing to the lower and more variable pressures obtainable, the waste produced, and the greater power consumption, increase the manufacturing cost.

Continuous mold presses, having a capacity of 50 tons per hour of 1 lb. briquets, are now on the market. It requires no more labor to operate one of these machines than a boulet press of 5 tons per hour, while it is evident the up-keep cost is much less per ton of briquets produced. Machines of this type permit nicer regulation of the mixture, resulting in a uniform product. The continuous mold type of plunger presses has been perfected in the United States; the machine combines the efficiency and exactness of the reciprocating plunger type with the continuity of operation and larger capacity of the Belgian machines. As the binder is the largest single item of cost, every effort must be made to reduce the amount necessary to insure merchantable briquets. In order to accomplish this, a perfect mixture of coal and binder, and a uniform temperizing of the agglomerate must be obtained.

Nearly every known substance having bonding properties has been tried as a briquet binder, but except in special instances, the only practicable one is pitch, which is made from tar recovered as a by-product in the destructive distillation of coal, from by-product coke ovens, or in carburetting water gas for illuminating purposes.

In spite of its general use, it certainly cannot be claimed that pitch is a perfect "binder." It is nearly all volatile combustible which produces smoke in burning; it usually gives off napthalene and other irritating and corrosive vapors that are injurious to the workmen, unless great care is taken in the manufacture of the pitch. On the other hand, pitch is distinctly a coal product and has the essentials of a good fuel; if properly made it is a good bonding agent; its melting point is such that the mixture can readily be "fluxed" with steam at atmospheric pressure, even though the pitch is hard; it is impervious to the action of water; a briquet made from pitch and non-coking coal and subjected to high pressure, will form coke in burning; pitch is cheap and available in all the manufacturing centers of the East and Middle West.

The objections are minimized when hard pitch is used; and this has the further advantage of hardening rapidly in the briquet so that ten minutes after the briquets are made they can be shipped or stored if properly cooled during that time.

There are local conditions in this country where other binders can be used more advantageously on account of the cost of coal tar pitch. On the Pacific Coast and in certain Rocky Mountain states, asphalt recovered from the distillation of petroleum furnishes an excellent binder, obtainable at a reasonable price. Attempts are being made to use crude petroleum as a binder by a process of rapid oxidation or the introduction of emulsifying and hardening agents. The same objection may be made to these as to the use of starch, sulfite pitch and other organic binders. The briquets require an additional treatment of drying or baking, which becomes very expensive in plants of large output. In Europe, where labor is cheap, some processes of this nature have met with success. Another objection to organic binders is that they are soluble in water, and the briquets must therefore be protected from the weather.

Except for the amount of impurities, all the coal from any mine has the same theoretical heating value. In order to increase the fuel value, and consequently the selling price of the coal, it is "prepared" for market by reducing or eliminating the impurities. This is accomplished by screening, washing or dry separation. The effective heating value is further increased by "sizing" the coal, and the nearer to uniformity of size, the better the results obtained. For this reason, great care is taken in "preparing" anthracite coal for market.

In the bituminous coal industry, the increased competition has forced operators to refinements of preparation which do not seem justified by the low selling price of the fuel. The coal is both washed and sized. Since the fuel value is practically uniform, there seems no good reason why the lump, egg, nut and pea should bring different prices, except that some of this coal is for industrial purposes, and some for domestic use. The coal which is handled several times before it reaches its destination, must be screened to meet market requirements. This means that the total value of the shipment has depreciated.

Another factor in the marketing of prepared coal is the unequal demand for the various sizes. The operator is a much stronger position if he has only one kind of product to sell. The conditions which prevail at our large distributing centers, like Superior and Duluth, illustrate this statement. In handling high grade coals like Pocahontas and New River, even the slightest preparation produces a large percentage of slack. The market for this slack is limited and the price low. In consequence it is difficult to realize enough more for prepared coal over the mine-run to pay for the lower selling price of the slack. Here is a situation which is met perfectly by briquetting the slack. The process converts a low priced coal, having a limited market, into a high priced domestic fuel for which the demand is unlimited.

One of the largest coal companies in this country has just completed at Superior, Wis., the largest briquetting plant on this side of the Atlantic for the briquetting of high grade bituminous West Virginia coal. The briquets are fast becoming established as a satisfactory domestic fuel and a keen competitor of prepared anthracite. By means of briquetting, the coal company is able to put on the market a much better preparation of lump and egg coal, and even carry this refinement to nut and pea sizes when the markets demand them, briquetting the surplus of fine coal, and greatly increasing the total revenue from all the coal. Briquetting also eliminates the probability of fire from the storage of fine coal on the dock.

Coal mined in the Pacific Coast states is of poor quality compared with that found in other sections of this country. The demand, however, is so great that the fuel brings a high price. The use of fuel oil on the Coast has made great inroads into the steam coal business, so that fine coal is a drug on the market. This situation years ago presented many features similar to the conditions upon which coal briquetting thrived in Germany. It gave an early impetus to our briquetting industry, and many plants were established. Because all the problems involved were not given due consideration, none of the plants has been a commercial success. Yet no section of the continent offers a better opportunity than is presented to the coal operators on the Pacific Coast today, for a modern briquetting plant properly designed and securely financed.

The same causes which led to failure of the Coast enterprises have produced similar results in other localities, and are but a repetition of experiences in England. The briquetting of coal is apparently so simple an operation that astonishing results are often obtained by the crudest apparatus. A few hand-made briquets serve unscrupulous promoters in organizing companies, selling stock and promising phenomenal returns. Unfortunately, coal is very cheap in this country, and the margin between slack from which the briquets are made and the lump with which they must compete, is so narrow that only very carefully designed plants of large output can produce briquets at a reasonable profit. Such plants must work in conjunction with established coal companies which are successful in the marketing of coal, and have ample supply of raw materials at their command.

As in any new business, the briquets must be introduced and the consumer educated to their use. The companies must be prepared to carry on the business, even at a loss, until the value of briquets is established, and the popular prejudice against any new product overcome. Many companies which were able to manufacture briquets after overcoming the mechanical difficulties, failed because they were not conversant with the commercial conditions, or because they ran short of funds before the briquets were established with the trade.

Practically all of the European railroads use briquets, and the quantity varies from 15 to 40% of the total coal consumed. The briquets for railway and steamship use are prismatic in shape. The French navy specifies 22-pound briquets. These briquets are broken before firing, and if well made will break into pieces without making dust. The railroads use briquets not to exceed 11 pounds in weight, which are fired one or more at a time, by hand. Storage fuel is usually in the form of briquets; they are carried on the tanks along with coal and generally used to get up steam, to make up time, or over heavy grades during the run.

The specifications to contractors furnishing briquets to the state railroads on the continent are very rigid, particularly in France. These specifications vary somewhat in the different countries, but are covered generally by the following items:

1st. Briquets shall be well made, sonorous, entire, with sharp edges, breaking with a clean-cut, brilliant and homogeneous fracture.

2d. Their cohesion shall be not less than 55% and they shall not soften at 50 degrees C.

3d. The briquets shall ignite easily without causing dense black smoke, shall burn with a quick bright flame and be consumed without disintegrating. The slag or clinker shall not adhere to the grates or tube sheets.

4th. The briquets shall not be hygroscopic nor contain more than 4% moisture. They shall contain between 15 and 22% volatile combustible, and not more than 11% ash. The coal shall have been freshly mined and free from sulphur.

5th. Coal tar pitch is the only binder specified; it must be practically odorless and the amount limited to 10%.

6th. The briquets must be prismatic with a square base;

when specified they are from 3 to 11 pounds in weight, according to kind of coal used, with a density of from 1.13 to 1.21.

These specifications regarding *quality* of briquets may be applied to requirements in this country. Prismatic briquets have not met with success here for reasons already mentioned.

Briquets and coal when burned in locomotives under the same conditions and at the same rate of combustion show an increased boiler efficiency of 15%, and and increased equivalent evaporation of 20% in favor of briquets. It has been thoroughly demonstrated that 25% more briquets than coal can be burned per square foot of grate surface per hour in a locomotive.

These results are attributed entirely to the physical characteristics of the briquets, as they show practically the same calorific value as the coal. The rate of combustion of any coal is limited by the air supply and the ability of this air to mix with the gases from the coal. When a lump of coal burns, the tendency is for the gases to pass off through the lines of least resistance; that is, from the crevices made in the coal as it breaks up in the fire. In the case of briquets there is no tendency to do this, owing to their homogeneous and porous structure.

If we examine a briquet in the process of burning, we find that it burns entirely from the outside. As the volatile combustible is driven off a layer of coke is formed which burns to ash and falls off or is carried away by the draft. Thus we find successive layers showing partial combustion of the fuel while the inner part is unaffected, and the briquet retains its identity as such until entirely consumed.

The density of the briquet is of prime importance. Harder briquets do not break up so easily and they burn more slowly in the fire. Thus the volatile combustible is driven off more nearly at the rate at which it can be burned with greatest economy, and the briquets form coke during the process of combustion even though made with an otherwise non-coking coal. This is more essential with high volatile than with high carbon coals.

Uniformity in size is the first consideration in obtaining economical combustion of any fuel. We have already noted the care which is observed for this reason in the preparation of anthracite. The market price of sized bituminous coal as against screenings or mine-run of equal calorific value, is another proof of this statement. Briquets are uniform in size and have the further advantage of remaining so until consumed.

The physical character of coal as delivered to the furnace, and its behavior in the fire, are often of more importance than its theoretical heat value. It is the usual experience that briquets make no objectionable clinker. The ash is finely divided and easily shaken through the grates. This is to be expected from the manner in which the coal is prepared before briquetting, and from the uniform distribution of the slag-producing elements of the ash, such as iron pyrites, throughout the briquet.

We often wonder why "lump" coal is so popular and brings such a high price. Certainly no one ever burns "lump" coal in his stove or house furnace or under his steam boiler. The locomotive comes nearest being an actual consumer of "lump" coal; but now the most progressive railroads are eliminating this idea by requiring that all the coal for use on their locomotives shall be crushed so as to pass through a 4″ or 5″ bar screen.

Undoubtedly this form of coal is demanded in the interests of the retail coal dealer who wishes to reduce his yard losses. When he comes to realize that the loss in handling the best "fancy lump" far exceeds that made in handling briquets, the newer fuel will come into its own.

The cleanliness of briquets is another important factor in their success as a domestic fuel. Smoke prevention is of universal interest, and has been the subject of a campaign of education throughout the country regarding the causes of smoke, in the burning of bituminous coal. Less effort is required to stoke a hand-fired boiler and maintain steam with briquets than with the commercial sizes of bituminous coal on the market today. This means that more opportunity is given to fire the boiler properly, get better and more economical combustion and greatly reduce the smoke nuisance.

When we consider that the railroads of the United States spend $200,000,000 annually for coal, any saving, however slight, is worthy of serious consideration. Even a saving of 10% on the coal stored by the railroads would represent a yearly economy of nearly $2,000,000. The item of greatest importance, however, is the economy which can be practised by the purchase and storage of briquets during the period of least demand for cars by the industrial world, and the use of the equipment for railroad purposes during that period.

The great complaint of the operator is the shortage of cars during the winter months. The difficulties of moving trains during this period of the year only add to the general discomfiture. Cars are tied up with coal in transit, or are held at division points as storage receptacles for railroad coal, when they should be earning revenue to their owners. Any unusual weather conditions work great hardships to the operator, transportation company and consumer.

European practice in the matter is assurance enough that briquets can be stored for long periods without appreciable deterioration, and experiments by the Government in this country show similar results. The degradation due to handling briquets to and from storage by modern mechanical appliances is much less than with the raw coal.

At the present time many of the railroads, particularly in the West, must purchase selected high grade Eastern fuels for storage purposes. This entails great expense for freight charges. If the storage fuels were carried in the form of briquets, lower grade coals could be utilized. Frequently these are near at hand and are the coals used daily for locomotive use. They cannot be stored without serious depreciation, and are frequently a total loss. Briquets made from these lower grade bituminous coals, (such as those mined in Indiana, Illinois and Kansas) show an evaporative efficiency equal to that of the best Eastern coals when used as mined. The saving which can be easily and directly reckoned from increased efficiencies based on cost of fuel alone, is enormous. The value in having an available fuel supply during mining and transportation interruptions; the value of briquets to increase the capacity of locomotives upon demand, and the liberation of coal cars for service, are economies none the less important because difficult to compute.

There is another phase of the briquetting industry which has not even seen the light in this country; namely, the use of lignite or brown coal, of which we have about 125,000 square miles.

The principal output of German briquets consists in those made from brown coal and manufactured in open mold machines without a binder.

Experiments in lignite briquetting have been carried on by our Bureau of Mines. The results show that only a small part of our lignites can be successfully briquetted in the German manner. The briquetting of the raw lignite after the practice of coal briquetting has been abandoned as futile. Considerable progress has already been made on a process for the partial distillation of the raw lignite, so that the resulting carbon may be manufactured into satisfactory fuel. No commercial plants have been built, but briquets made in experimental plants prove the possibility of producing a satisfactory domestic fuel. In the Dakotas, particularly, which aside from lignite have no fuel except that which is shipped in, any process which will utilize the lignite will be a great boon.

INDUSTRIAL CONDITIONS OF THE UTILIZATION OF NATURAL GAS

J. C. McDowell
Pittsburgh, Pa.

The Natural Gas Industry is a new enterprise peculiar to the United States and Canada, and has been wholly developed during this generation, for while its use can be traced back to lighting the village inn at Fredonia, New York, on the occasion of the reception of Marquis De Lafayette in 1824, its use did not assume any substantial commercial importance until 1882–1883 when natural gas began to be utilized extensively in the Pittsburgh region and to some extent elsewhere in Pennsylvania, both for domestic and for industrial fuel purposes.

Its growth has been phenomenal, and it now ranks with the great industries of this age; it is expanding with accelerated speed. The total value of gas consumed has increased from $475,000 in 1883 to $23,698,674.00 in 1900 and $70,756,158.00 in 1910. At this time, the total capital invested in the business is approximately $330,000,000.00 and this does not include the capital invested in collateral enterprises developed by the demand for material and supplies, created by the parent industry. The business has progressed from a precarious commercial enterprise to a science demanding skill of the highest order for its proper management.

Great improvement has been made in the past fifteen years in the methods of transporting, distributing and consuming natural gas. In this period cast iron pipe, with lead joints, has given place to steel pipe with rubber packed joints, hand regulation to automatic, a perforated pipe burner in a coal stove or furnace to modern appliances and today the most modern steam plants are being supplanted by natural gas engines.

A large army of keen inventive men with minds alert for improvements in their chosen business are making important changes in methods and devices so rapidly that it is difficult to keep pace with them.

A glance at the statistical report of the United States Geological Survey on the Production of Natural Gas in 1910, hereto attached, discloses the importance of the industry in thirteen (13) states and its existence in seven (7) states additional. It has also become an important factor in three (3) provinces in Canada: New deposits are being discovered and developed each year. It is the opinion of many persons qualified to speak on the subject, that the industry is still in its infancy and facts show the last year to be the maximum year in consumption and value of product sold.

It will be observed that Pennsylvania, the first state in which natural gas was used, still maintains the supremacy in volume and value of gas consumed, while Ohio is a close second. In the year of 1910, 1,327,722 domestic consumers in the United States were supplied with a daily average of 465,000,000 cu. ft. of natural gas at an average price of twenty-four and four-tenths (24.4¢) cents per cubic foot—an average daily equivalent of 23,250 tons of Bituminous Coal.

The saving to the consumer, in the use of gas, over coal is undoubtedly much greater than all the dividends declared by the corporations suppplying the gas and it is highly appreciated.

In the early years of development it was difficult to secure capital to carry on the business, then considered hazardous, but the steady growth and stability of the industry; the prosperity its production brings to a community and the profitable returns from natural gas investments for many years has compelled many financiers, once fearful of results, to realize that with conservative management they are among the best securities offered to the public.

The importance of the natural gas industry in the development of the country is realized by comparatively few, as its work is so unobtrusively done that it attracts no attention.

The Pittsburgh District, whose tonnage exceeds London, New York, Liverpool and Hamburg combined—undoubtedly owes its supremacy to the impetus given it by natural gas. The iron masters of Pittsburgh were saying that the iron business must go to the lakes to meet the ore, when in 1883 to 1885 natural gas superseded coal in practically every industrial plant in Pittsburgh. For six years gas was supplied in Pittsburgh and vicinity at from one third to one half the net cost of coal. New industrial plants multiplied until inability to secure suitable locations has been the only check to the growth of the region.

THE IRON AND STEEL INDUSTRY

Puddling Furnaces

In puddling furnaces, one ton of muck bar required forty (40) bushels of coal, costing about $2.00 per ton; gas was supplied at one-half that amount. In addition to the saving in the cost of fuel there was a large saving in repairs to furnaces, in handling coal and ashes and increased output.

Open Hearth Furnaces

In open hearth furnaces the fuel cost of steel was reduced from $1.00 per ton to 55¢. The quantity per week was increased fully twenty-five (25%) per cent and the quality improved over one per cent in sulphur analysis and the life of the furnaces prolonged. At the present time, a ton of open hearth steel can be produced with 5,500 cu. ft. of gas and nine melts can be made per week, as against six melts with coal. Open hearth furnaces using coal cannot successfully compete with natural gas at the present time.

Heating Furnaces

From tests made in heating a 160-pound pile, the saving in wastage in the use of gas over coal, is over 10%. There is also a great saving in handling coal and ashes and the life of the furnace is greatly prolonged, while the output from each furnace is greatly increased, equally good results obtained in all lines of iron and steel manufacturing; many iron and steel plants, by utilizing space otherwise required for handling coal, doubled their output.

THE PLATE GLASS INDUSTRY

In 1883, when natural gas was first used in the manufacture of plate glass, there were two small factories in the United States, with an output of about one million square feet per year, practically all our supply was imported, and its average price was over Two ($2.00) Dollars per square foot. The first plate glass plant using natural gas was built in the Pittsburgh District, in 1883 by the Pittsburgh Plate Glass Company. Then followed Tarentum, Ford City, Charleroi and Walton by the same company. Plants were also erected in Butler, Penna, and Ellwood, Indiana, all using natural gas. The Pittsburgh Plate Glass Company has owned its own supply from the first and now consumes over 10,000,000 cu. ft. daily in their own works in the Pittsburgh District and nearly as much in its works at Barberton, Ohio.

The development of this industry is directly credited to the natural gas. The total yearly output of the plants in the United States was over 40,000,000 sq. ft. in 1910 and the average price less than thirty (30¢) cents per square foot: Only about six million feet are imported and that in small sizes.

WINDOW GLASS

In addition to the saving in fuel value resulting from cheap gas supplied to window glass factories throughout the gas belts of the United States the saving in labor is greater in this industry than in any other. Its use greatly improves the quality of the glass and increases the output of each pot or tank: Practically all of the window glass factories in this country are using natural gas.

FLINT GLASS

The use of gas has greatly stimulated this branch of the glass industry, resulting in the keenest competition. Plants located in the gas district, where gas is very cheap are selling their product so low that factories not so favorably located for cheap gas are suffering. The glass products of the United States are selling in London at a profit at the same for which they are sold here, with freight added. The yearly product has grown from 80,000 tons in 1892 to over 300,000 tons in 1910.

BRICK MAKING

Natural gas has many advantages over any other fuel for brick making, other than its relative cost, particularly in the quality of the product, and the saving in waste brick. It requires an average of 8,000 cu. ft. of gas to burn one thousand paving brick. This industry has assumed enormous proportions throughout the middle west, where cheap gas is obtainable.

POTTERY AND TILE

Wherever suitable clay can be found in the vicinity of an ample supply of cheap natural gas, the manufacturer has a substantial advantage over competitors, not so favorably situated, in the superiority of his product and the reduction of the waste.

CEMENT AND SMELTING WORKS

The immense cement and smelting works of Kansas and Oklahoma owe their existence to natural gas, each cement works usually securing its own supply of natural gas and conveying it to its factory at the limestone quarry nearby.

For the past ten years the cement works of Kansas, have by reason of the cheap gas fuel near their works, had a monopoly of the business within reasonable freight rate areas to the extent of the capacity of their works.

The smelters of Kansas and Oklahoma secure their ores principally from the lead and zinc region of Kansas and Missouri. It is safe to say that the cost of gas to the cement works and smelters, and also to the brick yards in Kansas and Oklahoma for the past ten years has been less than 2½¢ per thousand cu. ft., equivalent to fifty cents per ton for coal.

GENERATING STEAM FOR POWER PURPOSES

The extent of the use of gas under boilers for generating steam for power purposes is determined by the price of coal in the furnace, compared with the price of gas, consideration being given to the increased capacity of gas fired boilers, comparative cost of attendance, economy of space and possibly quick firing to care for peak loads. In actual practice from 18,000 to 20,000 cu. ft. of gas under boilers is equal to one ton of the best Pittsburgh coal. This result can only be obtained by the installation of modern burners and expert boiler setting, consequently while there is at all times, a basic competition between the cost of natural gas and coal in the boiler furnace, the consumer is willing to pay a fair margin of difference in favor of natural gas for the advantages suggested.

INTERNAL COMBUSTION ENGINES

The gas engine development of the past twenty years has kept pace with the natural gas industry, with which it is most closely associated. In gas regions, where gas is regularly supplied for industrial purposes, gas engines are in very general use, particularly, for plants requiring 250 H. P. or less, and many large power plants are also equipped with gas engines.

The modern gas compressor stations installed by the gas companies for the purpose of taking the gas at low pressure from the wells and conveying it at high pressure, through long lines to distant markets are usually equipped with gas engines when large power is required, the units are frequently 1300 H. P. direct connected to compressors and are very efficient. Manufacturers of these engines now guarantee a consumption of only 9 cu. ft. of 1000 b. t. u. gas (when average quality of gas) per h. p. hour, when running at 75% of the rated load and 12 cu. ft. per h. p. hour is guaranteed in units of from fifty to 250 h. p.—as compared with the consumption of gas per h. p. hour in steam driven motors, the consumption of gas in gas engine practice is less than one third of the consumption by steam engines.

Notwithstanding, the increase of domestic consumption at times of maximum demand (in the winter) has taxed the limit of the pipe line systems to such an extent that industrial consumers cannot be supplied at all times, and many companies shut off all industrial consumption during the winter months.

The industrial consumption continues to grow. In 1910, 18,267 industrial consumers used 339,332,279 thousand cubic feet, an average of 929,000,000 cu. ft. per day, equal to 46,450 tons of bituminous coal. An impression prevails that gas is not now used to any extent in manufactures in the Pittsburgh district. When the business of the district is in a normal condition a volume of gas is consumed equivalent to 600 tons of coal daily. If the gas supply was shut off from the mills of the Pittsburgh District its business would be paralyzed, many of its factories would be compelled to move by reason of lack of space to handle coal and the inadequacy of the present railroad facilities, that are congested at times handling the finished product.

The manufacture of carbon black, (lamp black) from natural gas has become an important feature. The general principle in all of the methods used in the manufacture of carbon black from natural gas is that of incomplete combustion, a very wasteful method. A recent discovery of a method of decomposition is being experimented with at the present time and if operated on a commercial basis will probably revolutionize the carbon black industry.

The manufacture of gasoline from heavy gas, usually casing head gas, very seldom transported through lines to market is a comparatively new branch of the industry, utilizing a product heretofore wasted. As the price of gasoline advances the business will undoubtedly enlarge.

The appalling waste of gas is decreasing and there is now comparatively little to complain of except in Oklahoma and Caddo, where the terrible waste still continues, practically unabated, principally from wells producing both oil and gas. If the gas companies would engage to take this waste gas from the oil producers at a low price, and would equip their gathering systems in the field to receive such gas at a pressure which would not interfere with the operation of the oil wells, the waste from the principal source would be ended.

In many localities this arrangement could be made with profit to both parties, and when the oil producer can be shown a profit, the waste will cease.

The future of the industry, in most localities, seems secure for many years. The deposits in the devonian formation of the Appalachian region show slow decline. Many new reservoirs have been tapped and it is reasonable to expect deposits in lower horizons in many regions yet untried. Increased prices will result in a less volume of consumption, more careful use and consequent longevity of this matchless fuel.

The following table gives the distribution of gas consumed for industrial purposes in 1909 and 1910 by States:

DISTRIBUTION OF NATURAL GAS CONSUMED IN THE UNITED STATES IN 1910, BY STATES

State	Producers			Consumers		Gas Consumed		
	Reporting gas wells	Reporting gas from oil wells	Total	Domestic	Industrial	Quantity M. cubic feet	Domestic, Cents per M. cubic feet	Value
Pennsylvania.......	819	1,584	2,403	321,430	5,591	43,404,565	25.3	$10,972,250
Ohio..............	1,630	638	2,268	475,505	3,804	60,539,597	25.0	15,145,537
Kansas...........A	204	38	242	185,972	1,228	23,792,122	21.9	5,202,914
West Virginia.....B	241	189	430	86,778	2,823	13,637,059	17.4	2,377,276
New York..........	273	375	648	106,538	1,058	12,247,528	29.7	3,646,180
Oklahoma.........C	168	343	511	38,978	2,059	5,397,284	16.9	912,958
Indiana..........D	1,027	117	1,144	36,054	282	4,315,403	30.1	1,299,247
Kentucky..........	47	21	68	27,961	112	2,574,352	27.9	718,657
Illinois...........E	207	227	434	10,109	479	1,266,057	21.9	278,377
Louisiana..........	21		21	8,547	320			
Texas.............	19	20	39	14,719	133	1,616,332	31.8	514,782
Alabama..........	7		7	95	6			
California..........	30	124	154	8,292	217	245,738	79.2	194,631
Arkansas..........	9		9	4,422	121			
Colorado..........	5	11	16	1,051	13	722,895	24.8	179,324
Wyoming..........	5	2	7	353	4			
South Dakota......	37		37	371	8	23,074	77.6	17,899
Missouri...........	33	1	34	322	5	22,704	28.6	6,501
North Dakota......	14		14	212	3	16,620	39.8	6,610
Michigan..........	8	1	9	7	1	420	100.0	420
Tennessee.........	5		5	2		1,200	25.0	300
Iowa.............	5		5	4		80	50.0	40
Total	4,814	3,691	8,505	1,327,722	18,267	169,823,030	24.4	$41,473,903

GAS CONSUMED—Continued

State	Industrial			Total		
	Quantity M. cu. ft.	Cents per M. cubic feet	Value	Quantity M. cu. ft.	Cents per M. cubic feet	Value
Pennsylvania	125,470,994	10.3	$12,962,441	168,875,559	14.17	$23,934,691
Ohio	47,535,063	12.8	6,065,428	108,074,660	19.63	21,210,965
Kansas A	58,137,618	6.8	3,960,949	81,929,740	11.19	9,163,863
West Virginia B	63,430,697	5.1	3,240,634	77,067,756	7.29	5,617,910
New York	1,947,276	16.3	317,692	14,194,804	27.92	3,963,872
Oklahoma C	22,482,779	5.2	1,169,250	27,880,063	7.47	2,082,208
Indiana D	1,444,849	12.1	174,156	5,760,252	25.58	1,473.403
Kentucky	2,384,242	8.0	189,636	4,958,594	18.32	908,293
Illinois E	5,457,229	6.1	335,265	6,723,286	9.13	613,642
Louisiana Texas Alabama	6,494,170	6.8	441,901	8,110,502	11.80	956,683
California	2,518,769	11.2	282,066	2,764,507	17.24	476,697
Arkansas Colorado Wyoming	1,982,053	6.1	121,827	2,704,948	11.13	301,151
South Dakota	20,300	69.5	14,100	43,374	73.77	31,999
Missouri	24,440	25.0	6,110	47,144	26.75	12,611
North Dakota	1,000	40.0	400	17,620	39.78	7,010
Michigan	800	50.0	400	1,220	67.21	820
Tennessee				1,200	25.00	300
Iowa				80	50.00	40
Total	339,332,279	8.63	$29,282,255	509,155,309	13.90	$70,756,158

A Includes the consumption of gas piped from Kansas to Missouri.
B " " " " " " West Virginia to Maryland.
C " " " " " " Oklahoma to Missouri.
D " " " " " " Indiana to Chicago, Ill.
E " " " " " " Illinois to Vincennes, Ind.

THE DETERMINATION OF SOOT PRODUCED BY MINE LAMP OILS

Francis C. Phillips
University of Pittsburgh, Pittsburgh, Pa.

By act of the legislature of Pennsylvania approved June 9, 1911, a fixed standard was adopted for oils to be used in open mine lamps in this State, prescribing that such oils must not yield more than 0.11% by weight of soot when burnt in an open mine lamp and with a flame 1½ inch long. In this enactment the example of other states was followed, although there is here a departure from the common methods of attempting to secure the result desired.

In those states where coal mining is carried on, a necessity has arisen for strict control over the character of the oil used in open lamps. The regulations adopted in the chief coal mining states may be briefly stated in substance as follows:

The Laws in Other States

Illinois requires the use of a pure animal or vegetable oil or other oil as free from smoke as a pure animal or vegetable oil. The oil must not exceed 24° of Baumé scale (Act approved May 11, 1901).

Michigan requires that only an oil as free from smoke as a pure animal or vegetable oil shall be used for illuminating purposes in mines. This would exclude the use of paraffine in mine lamps (Act of 1909).

Ohio requires that mine lamp oils shall contain not more than 16% of mineral oil in admixture with animal or vegetable oils but the fatty oil so used shall not be less than 21½° nor more than 22½° Baumé and the mixture shall not exceed 24° Baumé. A special clause permits the use of paraffin wax (Act of 1911).

Indiana coincides with Illinois in its legal requirements regarding mine lamp oils.

Maryland requires the use of oils composed of 75% at least of lard oil, but prohibits the use of petroleum or its products. Paraffin wax is however permitted as an illuminant (Mining Laws of Maryland, Chapter 24).

Kentucky requires the use of a pure animal or vegetable oil or other material as free from smoke and bad odor and of equal merit as an illuminant as pure animal or vegetable oil. The specific gravity must not exceeed 24° Baumé (Act of 1906).

Montana directs that mine lamp oils shall contain not less than 84% of pure animal or vegetable oil nor more than 16% of mineral oil. It shall be of not more than 24° Baumé while the mineral oil component shall be between 34° and 36° Baumé, and the fatty oil shall be between 21½ and 22½° Baumé. Other material of equal merit as an illuminant may be used (Act of 1911).

Tennessee requires an animal or vegetable oil or one of equal merit which must have a specific gravity corresponding to 24° Baumé (Act of 1901).

Utah requires a pure animal or cottonseed oil or one of equal merit (Act of 1911).

Missouri requires a pure animal or vegetable oil or an oil of equal merit, and of not more than 24° Baumé (Act of 1899).

Oklahoma requires a pure oil as free from smoke as a pure animal oil (Act of 1908).

West Virginia directs the use of animal, vegetable or paraffin oil or other oil as free from the evolution of smoke as standard cottonseed oil (Act of 1901).

In all these instances, with the exception of Pennsylvania, it will be seen that no fixed standard of quality is adopted but the oil is required to conform in its qualities to those of an adopted standard oil, or to have a specified composition.

In all the ordinary applications of oils for illuminating purposes in the arts, it is possible to secure by proper methods of combustion an intensity of light comparable in quality with day light. The miner alone must be content to use a lamp in principle and effect the same as was used in ancient Babylon or at the present time by savage or half savage races. His difficulty lies in the one fact that his lamp can have no chimney.

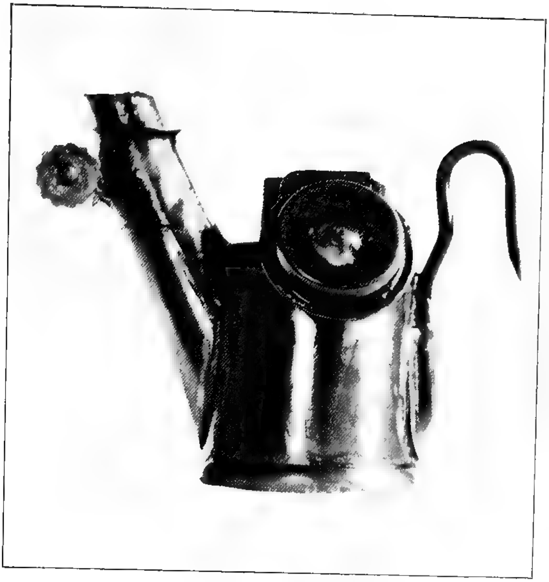


Fig. 1. The Lamp

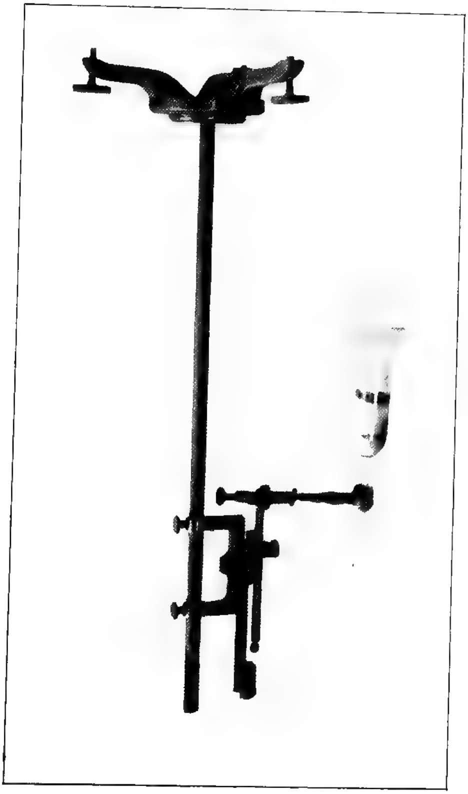


Fig. 2. Glass Soot Filter

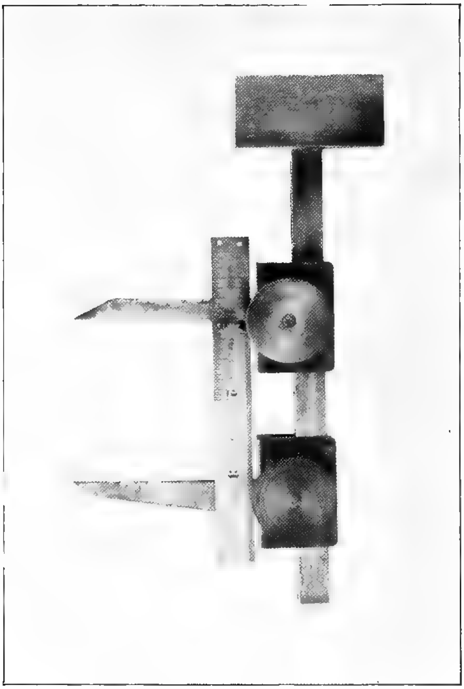


Fig. 3. Flame Measure

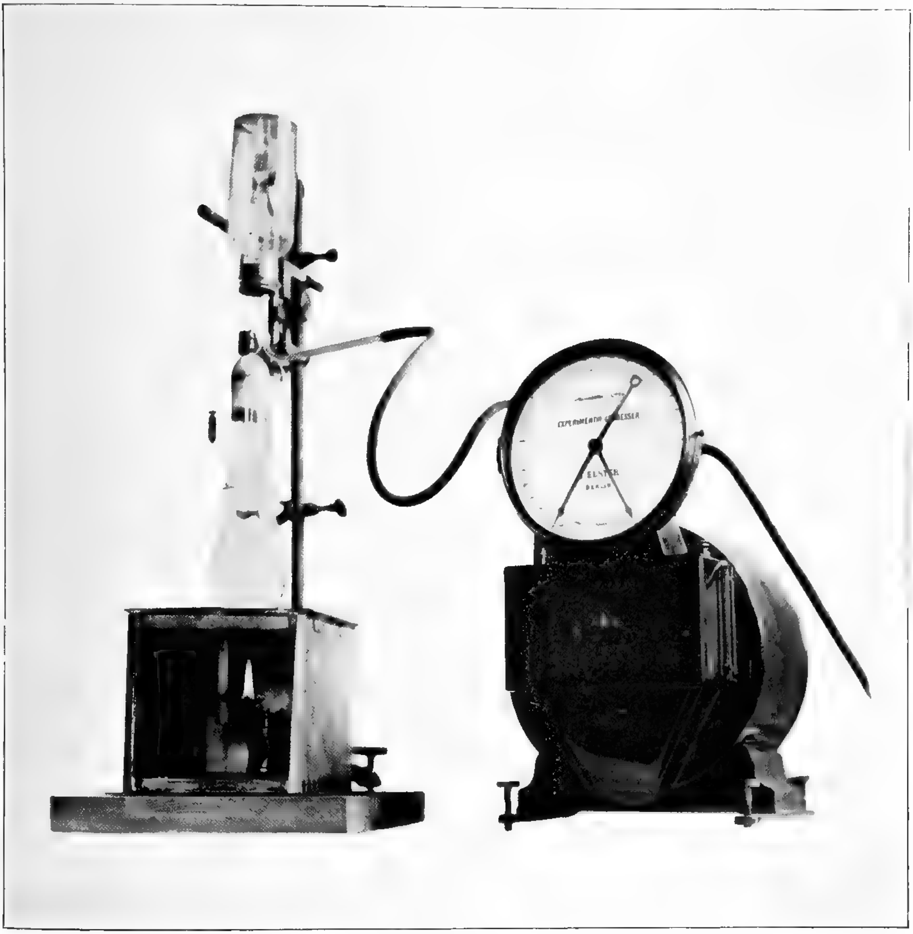


Fig. 4. Complete Apparatus for Soot Determination

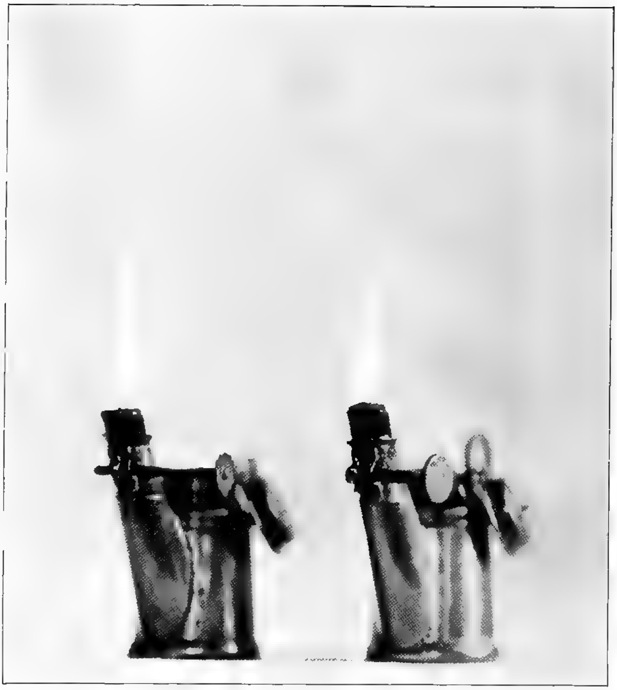


Fig. 5.

A Good Oil A Bad Oil

When two miners' cap lamps are filled, one with a high boiling mineral oil and the other with a good grade of vegetable or animal oil, and the flames regulated to a height of about 1¾ inches, a marked difference is noted in their appearance.

The animal or vegetable is brightly luminous and terminates above in a blunt or even rounded point. The mineral oil on the other hand, burns with a flame tapering rapidly to an extremely attenuated thread-like ending which is so thin and which merges so gradually into soot that the exact height of the flame is not easily gauged. The animal or vegetable flame is bright and clear. The petroleum flame is decidedly less bright, is of a dull reddish color and is apparently overloaded with soot. The sides of the Mineral flame are drawn together in a remarkable way directly above the wick (which in the lamps used was about ½ inch wide). From the upper end of the flame a column of soot escapes in the form of a sharply defined black thread which tends at a considerable height above the flame to disintegrate into a small cloud of soot particles.

This effect is not observed in the case of an animal or vegetable oil, but on lengthening the flame by raising the wick there is formed a kind of fringe of soot with a bundle of black threads pointing upwards. The flame produced by melted paraffin wax in a mine lamp is like that of an animal or vegetable oil, but brighter and is at present probably the brightest flame obtainable from a mine lamp. When lengthened to three or more inches these various flames behave much alike and are productive of the same clouds of soot.

These flames and more especially the petroleum flame, are readily attracted by solid objects and can be deflected or bent by a wire, a glass rod or other solid body.

A question arises here. Why does a highly combustible body in a condition of extreme fineness and in presence of excess of oxygen escape unburnt directly from a hot flame although susceptible to oxidation to CO_2 at a temperature below 300° C?

If this question could be answered we might be in position to burn the oils in open lamps in such way that soot production could be avoided. But not knowing how to restrain the tendency to soot production, we must try to select those oils which naturally possess this tendency in least degree.

The simplest way is to require the oil dealer to supply oils of particular composition or similar in its behaviour to some chosen standard oil. Probably the better way is to require an oil, safe as regards fire tests, and not exceeding a definite limit in soot producing power.

Mineral oils yield much soot as compared with fatty oils, but the fatty oils are apparently not susceptible of further improvement, while there is reason to expect that mineral oils may be improved so as to equal or excel fatty oils for mine use, and there is no objection to mineral oils except in so far as they contaminate the mine air by the evolution of soot. The ignorance of the miner which impels him to demand the cheapest oil for his lamp, regardless of quality is largely responsible for the character of the oils offered for sale.

The legislature of Pennsylvania has acted wisely in establishing a standard as to soot production rather than a standard of composition, as we should seek to encourage the refiner of petroleum to improve his oil to meet the requirements rather than exclude his products wholly from the market. It is probable however that the standard of soot production should be raised and that 0.05 instead of 0.11 per cent should be made the permissible limit. That the higher standard could be established without detriment to the refiner, there seems to be little doubt.

In an attempt to devise a method for the determination of the soot produced by an oil burnt in an open mine lamp, the following plan and apparatus were after much experimentation adopted.

The apparatus consists of a lamp in which a weighed quantity of the oil to be tested is burnt. The products of combustion are carried upward by a suitable suction pump and from the gain in weight of the filter, the proportion of soot per 100 parts of oil is determined.

1. The lamp. It seemed proper to use the ordinary open mine lamp, but made of brass and having a pinion to raise and lower the wick (See figure 2). The spout of the lamp used was 15 mm. wide at the open end. The wick used was 12mm. thick.

It is called "the Pieler wick." This was selected as being uniform in character and of convenient size. The lamp in use was filled with oil to within 5mm. of the top.

2. The soot filter. The lamp is placed so that the escaping soot is drawn upward into the soot filter. This is a glass tube 5 cm. long and 3.5 cm. wide with a flaring end below as shown in the diagram. This expansion is not absolutely necessary but desirable. The filter terminates above in a tube of 6mm. bore and 7 cm. long.

In the first experiments the filter was charged with asbestos as a filtering material. This was replaced by glass wool as the asbestos was found unsuited. Exposure of the filtering material, consisting of a finely fibrous silicate, to the hot steam from the flame causes a partial hydrolysis of the silicate. The effect of this heating was shown by first measuring the temperature in the asbestos filter by an electric pyrometer, while an oil lamp was burning beneath it. Then a small Bunsen gas flame was caused to burn for 1 hour at such height as to produce the same temperature in a filter. It was found that a newly charged and weighed asbestos filter placed over the same Bunsen flame for one hour, cooled in an exsiccator and weighed, had gained 0.12 grams in weight and it was only after heating the filter in the drying oven as described below, to a temperature of 130° that its original weight was restored. In the above experiment the purpose was to expose the glass wool to steam at the same temperature as in case of the oil lamp but with the omission of the soot. Glass wool was found to be better than asbestos. Quartz glass wool would be best of all, but its price prevents its use.

When German glass wool was used no difficulty occurred in bringing the filter back to its original weight.

In collecting the soot in the glass wool filter for weighing, there seemed to be danger of slowly burning it as it accumulated and was exposed to the heat from the lamp flame below.

The following experiment was then tried. A stream of purified air was led through a porcelain tube in which one gram of soot produced from a mineral oil had been placed. It was found that the escaping air stream caused a precipitation in lime water when the temperature of the furnace rose to 300° C. At a higher temperature decided indications of Carbon Monoxide were obtained. The air stream escaping from the porcelain tube produced a black precipitate in a solution of palladium chloride, this being followed by a reaction in lime water. It was found that CO_2 was formed when the temperature of the combustion tube was raised to 250° C. and in repeated trials the temperature of incipient CO_2 formation was found to be between 250° and 300°. The reaction became stronger as the temperature rose, but at a temperature of 800° the oxidation was still a slow process. CO was produced in small quantity at 400° and increased very little while the temperature rose to 800°. This fact is of interest as it has been frequently asserted that CO can only result from oxidation of carbon at very high temperatures. The filter contains a layer of fine glass wool 6 to 8 cm. in depth and supported by a tight fitting disc of nickel gauze.

3. The Lamp Flame. In order to measure the height of the flame, the device shown in figure 3 is used. The two side arms are independently movable by rack and pinion past an inch scale, permitting of accurate measurement.

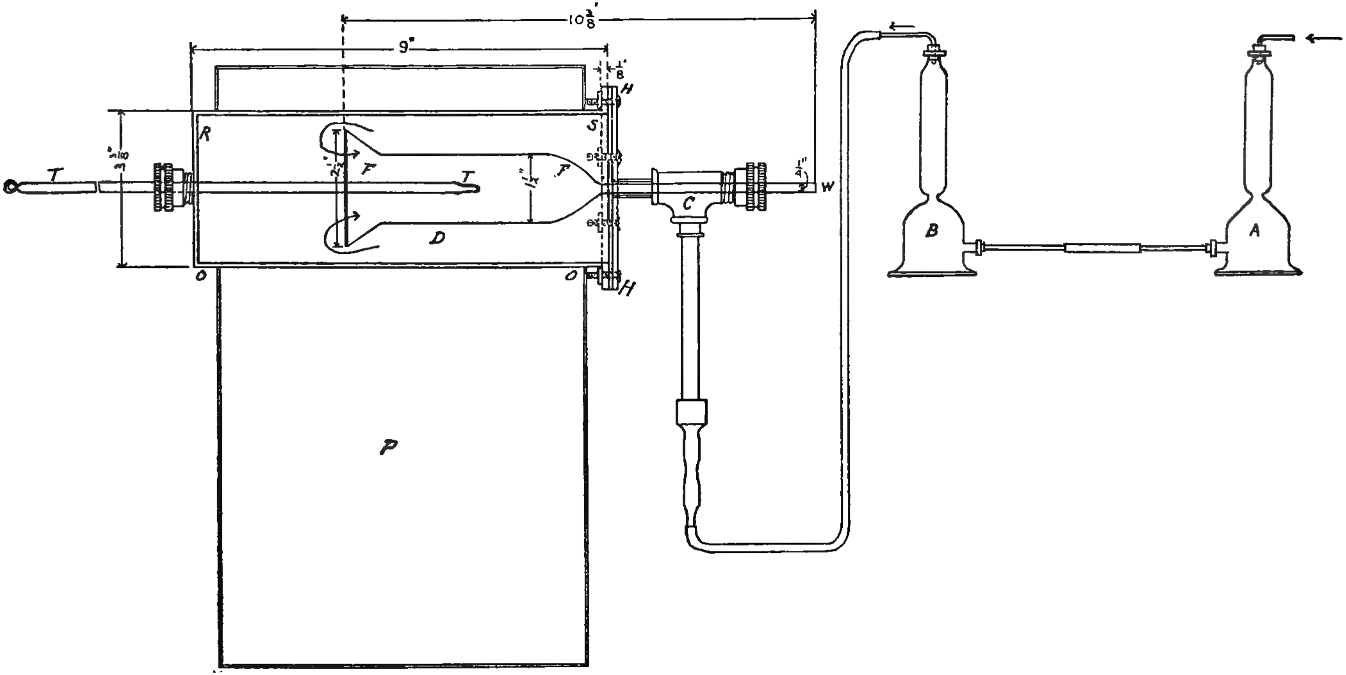
4. The tin box shown in figure 4 is used to guard against draughts of air which greatly disturb the flame.

5. The filter connects above with an inverted bottle containing a piece of white filter paper. Blackening of this paper would indicate that soot had been drawn through the glass wool and had been lost.

6. The gas meter used renders it possible to control the rate of air flow, as it is important that the rate be insufficient to promote combustion, but sufficiently rapid to draw the soot away from the flame.

7. Suction pump. Any convenient form of suction pump of sufficient capacity may answer. A large Richards pump was used in the experiments described.

8. The Drying Oven. A brass cylinder RS, 22 cm. long and having a diameter of 10 cm. is closed permanently at the end R and at the other end by a brass plate bolted to a flange as shown. Air dried by two calcium chloride jars is drawn by way of the brass T tube C into the oven and passes through the glass filter held in place as shown. A thermometer T is placed in the filter.


10 3/8"
9"
1/8"
H
S
R
T
T
F
F
D
2 1/2"
1 1/2"
3 1/10"
O
O
H
C
1/4"
W
P
B
A

A suction pump (not shown) is connected with the narrow stem of the filter at W.

PROCESS OF DETERMINATION

The burning of the lamp is continued for 1 hour, which means the consumption of 5–8 gm. of oil in most cases. The filter is dried in the oven at 130° C. for 1 hour. It is then cooled and left in an exsiccator for ½ hour. It is then weighed and placed in position. A current of air at the rate of 200 liters per hour is drawn up through the filter and measured by the gas meter, the gas meter being run by suction. The filter is replaced in the oven and heated for 1 hour to 130°, when it is cooled in an exsiccator and weighted.

Refined vegetable and animal oils yield much the same amounts of soot, often less than 0.01% of the oil consumed.

Petroleum oils yield more than 0.1% and sometimes as much as 1% or more of soot, as determined by the above method.

In the determination the chief difficulty has been found in regulating the flame height. Certain oils fluctuate incessantly in flame height. Others burn with great uniformity. The inferior sooty oils yield generally, but not always, the less steady flames.

No attempt is made in this paper to define the composition of soot and I have taken the term to mean merely the black substance emitted by certain flames, although in its determination the moisture which it carries has been eliminated by a process of drying before it is weighed.

Probably we should, if it were possible, include in the determination the *entire soot particle*, moisture and all, which enters the mine atmosphere.

(*Abstract*)

THE COMPOSITION OF NATURAL GAS

Francis C. Phillips

This paper contains the result of an examination into the composition of natural gas as learned from published analyses and from the study of reactions of these various constituents. The probability exists that many published analyses are to some extent in error concerning some of the constituents owing to inherent defects in recognized analytical methods, leaving doubts as to the presence of constituents important to a study of the general problem. An attempt is made to show that a more exhaustive study is called for in order that a conclusion may be ultimately reached in regard to the mode of genesis of natural gas, and that the measures to be taken for the conservation of this valuable fuel must be determined eventually by our ideas as to its genesis as affecting the durability of the supply.

UEBER DIE BEZIEHUNGEN ZWISCHEN DER CHEMIE DER ERDOLE UND DER GEOLOGIE DERSELBEN

M. A. Rakusin
St. Petersburg, Russia

Meine Herren!

Die syntetische Chemie des Erdöles, um die sich Männer, wie *Markownikow*, *Beilstein*, *Mabery*, *Richardson*, *Poni*, u. A. hoch verdient gemacht haben, hatte eine *Klassifizirung der Erdöle nach der Zusammensetzung der sie bildenden Kohlenwasserstoffe* zur Folge, eine Klassifizirung, die mit der *Provenienz* der Rohöle im Zusammenhange steht. Für den syntetischen Chemiker genügte es ein einziges Erdöl aus irgend einer Fundstatte zu untersuchen, um den Charakter der Kohlenwasserstoffe festzustellen. So spricht z. B. *Markownikow* von der Untersuchung des "Kaukasischen Erdöles," *Popovici—vom* "Romänischem Petroleum" u. s. w.—-Man begnügte sich mit solchen Definitionen, obgleich man vielfach ahnte, dass auch in ein und derselben Gegend, aber in verschiedenen Punkten, oder in verschiedenen Tirfen das Rohöl grundverschiedene Eigenschaften aufweist. So kannte man seit Jahren die Unterschiede in der Zusammensetzung der Erdöle aus Balachany und Bibi-Eybat, Swjatoi Ostrow und Surachany, oder Bustenary und Campina, die bekanntlich nur wenige Kilometer von einander entfernt sind; auch ahnte man, dass das Erdöl aus ein und derselben Fundstätte in verschiedenen Tiefen verschiedenes spez. Gewicht bezw. verschiedenen Destillatgehalt aufweist; man versuchte aber nicht hieraus irgend welche chemisch-geologische Schlüsse zu ziehen. Die Chemiker und Geologen gingen verschiedene Wege, arbeiteten unabhängig von einander, und eine gegenseitige Unterstützung lässt sich nur ausnahmsweise merken.

Ganz anders gestaltet sich die Art der exakten Erdölforschung seit 1904.—In diesem Jahre glückte es mir nicht nur die optische Aktivität und zwar *Rechtsdrehung* des Balchanyschen Erdöles und seiner Derivate festzustellen, sondern auch zu beweisen, dass *die meisten Erdöle der Welt diese merkwürdige Eigenschaft aufweisen.*

Hiermit war der erste Grundstein der *physiko-chemischen Erdölgeologie* gelegt. Die Frage, *woraus* das Erdöl entstand, ist also experimentell gelöst: die Erdöle sind ausschliesslich *organischen* Ursprungs. Die Karbid-Theorie von *Mendelejew* u. A. gehört nunmehr der Geschichte, und selbst der geniale Begründer dieser Theorie, zu dessen Lebenszeiten die optischev Aktivität des Erdöles bewiesen wurde, vermochte nichts neues zu Gunsten der wiederiegten Theorie auszusprechen.[1]

Von noch grösserer Wichtigkeit waren die verschiedenen *Konsequenzen,* die sich aus der optischen Aktivität der Erdöle ziehen liessen.—Zunächst wurde festgestellt, dass die Erdöle in dieser Beziehung an die *ätherischen Oele* erinnern, eine Tatsache, die für die Frage nach der Genesis des Erdöles von unzweifelhafter Bedeutung ist.—Alsdann bei den Versuchen *die optische Aktivität der dunkel gefärbten Rohöle in verdünnter Lösung* (C6H6 etc.) festzustellen, ergabsich die merkwürdige Tatsache, dass *Röhole oft in den verdünntesten Lösungen von* 1/64% *für den polarisirten Lichtstrahl* (nicht für den Sonnenstrahl) *undurchlässig sind.* Offenbar sind es *die kohligen Substanzen,* die im Erdöl allerfeinst suspendirt sind, und *dem polarisirten Lichtstrahl gegenüber sich, wie feste Körper verhalten.*

Da aber Rohöle verschiedener Herkunft den polarisirten Lichtstrahl bei verschiedener Konzentration durchlassen, also verschiedene *Karbonisationskonstante* aufweisen, wie ich mich speziell ausdrückte, so ist es klar, dass diesem verschiedenen Verkohlungsgrade der Rohöle auch verschiedene *Verkohlungsperioden* (Karbonisationsperioden) entsprechen müssen. In jeden erdölbildenden Prozess ist mithin ausser der *Bildungsperiode* (b) auch die *Verkohlungsperiode* (v) einufzühren. Der einfachste Ausdruck für das *geologische Alter* (A) eines Erdöles wäre also folgender: $A = b + v$.

In diesem Ausdruck ist v eine bereits messbare Grösse, und zwar bilden *die Karbonisationskonstanten das relative Mass fur die Verkohlungsperioden.*

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[1] Es ist hierbei ausdrüscklich betont dass ich die Arbeit beumann die Richtigkeit der Karbod-Theori zu beweisen; ich kam aber zu entgegngesetzen Resultate.

Kurz nach der Veröffentlichung dieser Ansichten[2] ersuchte mich das Geologische Kommité zu St. Petersburg meine Arbeiten, die damals nur 6 Erdöle betrafen, auf zahlreiche Rohöle der verschiedensten Fundorte Russlands auszudehnen.—Es war das, so viel bekannt ist, der erste Fall einer gemeinsamen Arbeit von einem Chemiker mit Geologe und überflügelten die erzielten Resultate, wie wir bald sehen werden, jede Erwartung.

Unter Zuhülfenahme des *Dayschen* Filtrationsprinzips wurde der Begriff von *korrespondirenden Erdölen* an jeder beliebigen Fundstätte festgestellt, ein Begriff, der es ermöglicht nach den gegebenen Eigenschaften eines Rohöles von bekannter Lagerungstiefe die Eigenschaften der zugehörigen Rohöle oberhalf und unterhalb dieser Lagerungstiefe *vorauszusagen.*[3] Und tatsächlich haben sich diese *Voraussagungen* sich vielfach *bestättigt*, so z. B. in *Surachany*, wo über 40 Jahre vergebens nach dunklem Rohöle gebohrt wurde, und am 14-ten November 1907 ein Springer dunklem Rohöles entstand. Die Bohrung wurde nämlich auf das dringende Anrathen des ausgezeichneten russischen Geologen *Golubjatnikow* fortgesetzt, der bekanntlich mit mir parallel die Erdölfunde des Kaukasus geologisch erforschte.

Auf den Begriff des *geologischen Alters* zurückkommend, will ich sagen, dass der Ausdruck für dasselbe in seiner allgemeinsten Form der folgende wäre:

$$A = b + r + v + z,$$

wo r—die *Razemisationsperiode* und z—die *Zersetzungsperiode* bedeuten.

Die Tatsache, dass die meisten Erdöle der Welt ziemlich hohe optische Aktivität aufweisen, schliesst eigentlich die Möglichkeit von Razemisation, und erst recht von Zersetzung im erdölbildenden Prozess aus, und wurden die Grössen r und z, wie gesagt, nur der Allgemeinheit wegen in die Gleichung eingeführt. In dieser Form nennen wir diese Gleichung *die erste Gleichung der physiko-chemischen Erdölgeologie*, die die *chemische Statik* der Erdöle interprätirt, während die Gleichung $A = f + r + v + z$ auch dir *geomechanischen Faktore* '(zunächst die Filtration) in Betracht zieht.

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[2] Journ. d. russ. phys.-chem. Ges., 1906, *pp*. 790–799.

[3] Bul. du Com. Geol. de Russie, 1906, pp. 472–478.

Beide Gleichungen zusammen geben die Möglichkeit *die ganze Mannigfaltigkeit der Erdöle in der Natur theoretisch abzuleiten.*

So entsprechen z. B. *die meisten Erdöle des Bakuer Distrikts* da sie unzweifelhaft Filterdestillate eines zugehörigen Muttererdöles und nicht razemisirt, also erst recht nicht zersetzt sind, der Gleichung: A = f + v, wo beide Summanden, wie wir sehen, messbare Grössen sind.

Besonders einfach und lehrreich ist die Gleichung für das geologische Alter *des lichten Rohöles aus Surachany.* In diesem Falle wird auch die Grösse v = o, da das Rohöl keine Verkohlungsprodukte enthält (K/100%). Die Gleichung gestaltet sich sonach, wie folgt: A = f.

Die Frage nach dem geologischen Alter lichter Rohöle ist also im Allgemeinen lediglich eine Frage der subterranen Hydraulik.

Wir haben heutzutage genügende Begründung zu behaupten, dass die zukünftige Naphtageologie ihre Haupterfolge der richttigen Deutung *der optischen Aktivität der lichten Rohöle und ihrer Derivate* und der *Undurchlässigkeit der Lösungen von dunklen Rohölen*[4] *gegenüber dem polarisirten Lichtstrahl.* zu verdanken haben wird.

Besonders lehrreich erscheinen schon jetzt die Schlüsse, die sich aus dem Zusammenhange zwischen den Lagerungstiefen korrespondirender Erdöle und ihren Karbonisationskonstanten sowie anderen physiko-chemischen Konstanten ziehen lassen.

So hat es sich bei der Untersuchung von etwa 120 Erdölen des Kaukasus u. anderer Gegenden herausgestellt, dass: *das spezif. Gewicht mit der Tiefe zunimmt, während die Verkohlungskonstante abnimmt*[5] *Gleichzeitig nimmt der kalorische Effekt*[6] *der korrespondirenden Rohöle mit der Tiefe ab:* schliesslich liess es sich feststellen, dass *bei korrespondirenden Rohölen auch die Ausbeuten an gleichnamigen Fraktionen im Zusammenhange mit den Lagerungtiefen stehen.*[7]

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[4] Ubrigens lassen ich dunkle. Rohole, durch Fullererde. etc. leicht entfräben.

[5] Bul. du Com. Geol. de Russie, 1906, pp. 299–313.

[6] Ibidem, 1908, pp. 407–427.

[7] Journ. d. russ. phys.-chem. Ges., 1909, pp. 483–500.

Diese wichtigen Gesetzmässigkeiten geben die Möglichkeit einer seits die Eigenschaften der Rohöle in irgend einem Komplex an jeder beliebigen Tiefe *vorauszusagen*, und andererseits die Frage zu beantworten, an welcher Tiefe die physiko-chemischen Konstanten von einem der Rohöle im Komplex eine gegebene Grenze erreichen.

Dieser Umstand und die von *Golubjatinkow* festgestellte Tatsache, dass die Temperaturen in korrespondirenden Rohölsonden dem geotermischen Gradient nahezu entsprechen, trug zur Klärung der alten und doch immer neuen Frage über den *Zusammenhang zwischen Vulkanismus und Erdölbildung* bei. Es ist doch nämlich klar, dass unterhalb der *Zone des festen Muttererdöles* sich folgende Zonen in successiver Reihenfolge unterscheiden lassen müssen: *die Erweichungszone der Bitumina*, die *Schmelzzone*, die *Siedezone*, die *Razemisationszone* und schliesslich die *Zersetzungszone*, unterhalb deren *die Sphäre der vulkanischen Erscheinungen* beginnt. Mithin sind *die Prozesse der Erdölbildung und des Vulkanismus räumlich und zeitlich von einander getrennt, und von einem direkten Zusammenhange zwischen Erdölbildung und Vulkanismus kann keine Rede sein.*[8] Das ist auch klar, denn: 1) könnten optisch aktive Erdölderivate bei der Temperatur der Vulkane nicht existiren, und 2) beweisen uns die geotermischen Messungen in den uns zugänglichen Tiefen, dass die erdölbildenden Prozesse sich tatsächlich bei relativ niedren Temperaturen abspielen, Temperaturen, deren Zuwachs mit der Tiefe sich annähernd berechnen lässt.

So kamen wir wiederum zu einem wichtigen chemisch-geologischen Schluss, der beim Beginn unserer Arbeiten nicht einmal geahnt werden konnte.

Ehe ich nun meinen Vortrag schliesse, muss ich bemerken, dass ich mit Rücksicht auf die kurze Frist, die hier jedem von uns zu Gebote steht, nur auf das wesentlichste hinwies. Noch eines möchte ich nicht unerwähnt lassen: namentlich des *Zusammenhanges zwischen dem Paraffingehalt der korrespondirenden Erdöle under deren Lagerungstiefen. Der Paraffingehalt nimmt mit der Tiefe ab.* Auch diesen Schluss gewann ich auf polarimetrischem Wegel,[9] und späterhin stellte es sich heraus, dass *Gilpin* und *Cram*[10] im Laboratorium des unermüdlichen *Day zu* ähnlichem Schluss auf chemischem Wege kamen, während eine ganze Reihe von Früheren Geologen,[11] und neuerdings auch der hochverdiente *Strijow* in Grosny, die notwendigen geologischen Belege hierfür fanden.

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[8] Ibidem.

Meine Herren! Bereits in der zweiten Hälfte des vorigen Jahrhunderts sagte der berühmte englische Physiker *Jellet;* "*Kein Gebiet der Wissenschaft scheint dem Forscher wichtigere Ergebnisse zu versprechen, als die Anwendung der Optik auf die Chemie. Schon hat die optische Wissenschaft dem Chemiker die Lösung von Problemen gegeben, deren Erforschung sogar ausserhalb seines Bereiches zu liegen scheinen.*"

Ich glaube annehmen zu dürfen, dass diese *Worte Jellets* in Bezug auf die optische Chemie des Erdöles ihre volle Geltung haben, und dass die Fortsetzung unserer Arbeiten auf diesem dankbarem Gebiete noch reifere Früchte zeitigen wird.

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[9] Ber. d. deutsch, chem. Ges., 1909.

[10] *M. Rakusin.* Die Polarimetric der Erdöle(Berlin, 1910), pp. 275u.ff.

[11] Ibidem.

(*Abstract*)

APPLICATION OF THE DIMETHYL SULPHATE TEST FOR DETERMINING SMALL AMOUNTS OF PETROLEUM OR ASPHALT PRODUCTS IN TARS

Charles S. Reeve and Richard H. Lewis

This paper, after briefly reviewing the literature on the dimethyl sulphate test, notes that the best method to date fails to detect the presence of open-chain hydrocarbons in tar-asphalt mixtures when the asphalt or petroleum is ten per cent or less of the mixture. Commercial specifications are now being drawn which require less than ten per cent of asphalt in mixtures with tar.

The authors proceed to show that as low as three per cent of asphalt or petroleum can be detected in these mixtures by making the dimethyl sulphate test on higher boiling fractions (315°C–350°C and 350°C–370°C). Tables of experimental data are given.

The results do not give any absolute idea of either the amount or exact nature of the material which has been fluxed with the tar. It is thought possible, however, that the improvement which has been made in the test will enable the chemist to ascertain whether his specifications are being fulfilled, by checking up the material supplied against laboratory mixtures of the same amount and grades of materials required.

PETROLEUM ANALYTICAL METHODS

S. P. Sadtler
Philadelphia, Pa.

The object of this paper is to discuss the following:—Can the presence of oxygen in Petroleum and Asphalts be established by a direct method of ultimate analysis?

To get the full import of this question, a few words of introduction are needed, bearing upon the subject of what those interested in the chemistry of petroleum and asphalt know with regard to this matter of the presence of oxygen in substances of these two classes.

Hoefer (Das Erdoel und seine verwandten, 2nd Auf. Seiten 55 und 56) gives a list of 59 ultimate analyses of petroleums from all countries. It is true that more than half of these are the earlier analysis of St. Claire Deville and Boussingault in which only carbon and hydrogen were determined and the balance needed to make 100 was assumed to be oxygen, but in a large number of more recent analyses both the sulphur and the nitrogen when present have been directly determined and the balance then ascribed to oxygen. Notably in Russian Oils and Japanese Oils, both analyzed in recent years and noting the sulphur and nitrogen, has this presence of oxygen been recorded.

Rakusin (Die Untersuchung des Erdoels und seine Producte. 1906, p. 77) also quotes more recent analyses of Russian petroleums by Charitschkoff and by Nastjukoff, who find from 0.4 to 2.5% of oxygen and what is of interest, note that the percentage of oxygen increases in the heavy petroleums and residues with the specific gravity.

But we are not obliged to base our belief on the presence of oxygen in petroleums on calculations made from ultimate analyses. The discovery of the petroleum acids by Hell and Medinger in Roumanian oils and phenols and of the naphthene-carboxylic acids by Markownikoff and Oglobin has given us an explanation of the presence of oxygen and justified the assumptions made from the ultimate analyses.

With the natural asphalts, the case is different from that of petroleums. Although earlier ultimate analyses of asphalts gave large percentages of oxygen, it was because the presence of sulphur in them had not been recognized and the oxygen was supposed with the carbon and hydrogen to make up the ash-free bitumen. However, Köhler (Chemie und Technologie der Natürlichen und Künstlichen Asphalte, 1904, p. 81) gives several analyses of natural asphalts by Day and Bryant and by Kayser in which a small percentage of oxygen is given as present alongside of a larger percentage of sulphur.

Both Clifford Richardson andPr of. S. F. Peckham, eminent American authorities on asphalt, have taken the position that not only is sulphur a distinctive element for natural asphalts, but equally that oxygen is to be considered as foreign to natural asphalts.

Besides the natural asphalts, we have also to note the artificial asphalts, obtained from petroleum, either by simple removal of the volatile portions or by some form of treatment with oyygen or sulphur at high temperatures. To the first class belong such products as "D grade Asphalt," made from California asphaltic petroleum, (Clifford Richardson. The Modern Asphalt Pavement 2d. Ed. 1908, p. 263) and "Baku Pitch" (Ibid p. 271) and to the second class Ventura Flux, Byerlite and Sarco Asphalt. Of these last mentioned products Byerlite and Sarco Asphalt have been made from liquid petroleum-residuums by the action of a current of air, either drawn through or forced through at temperatures ranging from 380° F. (193.3° C.) to 500° F. (287.7° C.)

The action of the heated air may have two different effects (see Höfer p. 85) according to temperature and rapidity of quantity of air passed through. The oxygen may cause splitting off of hydrogen in the form of water, with condensation of the hydrocarbons affected, or the oxygen may be fixed, forming products of oxidation which remain, in either case resulting in thick semi-solid or solid products. Not only would it be very desirable from a scientific point of view to determine which of these reactions has taken place, or whether both have united in the formation of the solid asphalt-like products obtained, but the matter has been the subject of investigation in connection with patent litigation over rival processes.

Of course, direct determinations of carbon, hydrogen, sulphur and nitrogen may and do leave varying deficiencies to be charged up to oxygen, but it would be desirable to be able to confirm these calculations by a direct determination of the oxygen in the product. No such method has thus far come into common use. The method of Baumhauer, neither in its earlier form nor in its later form, using a weighed quantity of dry silver iodate and requiring first a current of hydrogen, then of nitrogen and finally of hydrogen again, has not been favorably commented on by those who have tried it. The method of Mitscherlich of burning with mercuric oxide is also intended to give the oxygen at the same time that the carbon and hydrogen are obtained, but this method does not seem to have worked satisfactorily in the hands of those who have referred to it and has not been adopted by chemists.

The process which I desire to present to those interested in this subject is very simple in theory, although its execution is not free from difficulties and requires time for its proper completion. It is primarily the invention of Dr. Wm. M. Cross, City Chemist of Kansas City, Mo., with whose permission I have worked upon it with a view of making it applicable to this class of products, and to whose courtesy I am also indebted for the permission to give publicity to these results. It consists in a combustion carried on in a current of dried and purified hydrogen gas, the front of the combustion tube being filled with iron wool, which, brought up to a bright glow and thoroughly reduced by the hydrogen, then acts as contact-substance and brings about complete reaction between the hydrogen and the vapors given off from the decomposing petroleum or asphalt, whereby any oxygen present is taken up in the form of water vapor, passing on to be absorbed ultimately in a weighed chloride of calcium tube. In making the determination, hydrogen is passed very slowly through strong sulphuric acid, calcium chloride and over phosphorous pentoxide into the end of the combustion tube containing the boat with the weighed asphalt sample, beyond which is a sufficiently long layer of iron wool. The combustion tube at the farther end is connected with a good-sized U-tube containing purified asbestos wool or preferably spun glass and this to a weighed chloride of calcium tube for absorbing water. When the combustion furnace is first lighted, only that part of the tube containing the iron wool is strongly heated, the part containing the asphalt being kept cool. Hydrogen is then passed very slowly through the apparatus until the chloride of calcium tube used for collecting water has come to constant weight and so remained for some time. The part of the tube containing the asphalt is then increased in temperature very gradually until ultimately the boat and its contents are heated to the maximum temperature attainable and so held for a time. If the large U-tube containing the asbestos or glass-wool is kept cool, no condensable vapors pass beyond, and if the current of hydrogen be continued a sufficient length of time after the full heat has been applied, it will take all water through as vapor into the weighed chloride of calcium tube. No trouble need be anticipated from the small amount of sulphur contained in the asphalt or petroleum product, because the heated iron wool is capable of taking it up, in whatever form it is liberated.

After beginning my trial of the process with ordinary combustion tubing, I was led by reason of the necessity of keeping the portion of the tube containing the boat with the weighed asphalt cool, while the portion containing the iron wool had to be heated to a bright red heat, to try a tube of fused silica and have found this to possess great advantages. With a tube of transparent fused silica, some 30 inches in length, which I obtained from the Silicate Syndicate Ltd. of London, Eng., the iron wool can be brought to the desired heat, while the end of the tube containing the boat can be kept perfectly cool by water trickling upon it. By this means the rubber corks with which the ends of the combustion tubes are fitted can also be kept cool so that no overheating can take place.

I have not yet completed my analytical work upon the material taken to try out the method and prefer to reserve a complete illustration of the applicability of the method to both petroleums and asphaltic substances for a fuller paper. I will, however, give two oxygen determinations in a blown petroleum-residuum, or so-called artificial asphalt.

Determination of Oxygen.	I.	II.
Weight of material taken	1.0065 grms.	0.9767 grms.
Water absorbed in Ca cl_2 tube	.0440 grms.	0.0394 grms.
Corresponding weight of oxygen	.0391 grms.	0.0350 grms.
Percentage of oxygen	3.88%	3.58%

NEUERUNGEN AUF DEM GEBIETE DER DESTILLATION HOCHSIEDENDER OELE

LEO STEINSCHNEIDER
Brün, Austria

Ich habe es mir zur Aufgabe gestellt, Sie in grossen Zügen mit den Fortschritten bekanntzumachen, welche auf dem Gebiete der Destillation des Rohöles, unter besonderer Berücksichtigung der Destillation hochsiedender Oele, im letzten Jahrzehnt in Oesterreich gemacht wurden.

Ich will gleich bemerken, dass diese Entwicklung in Oesterreich zum grossen Teile unabhängig von der anderer Länder gegangen ist, weil sie sich notgedrungen auf anderen Linien bewegen musste. Die Ursache hiefür liegt darin, dass der Markt an die Fertigprodukte stets steigende Ansprüche stellte und dass der öesterreichischen Industrie nur ein parraffinhältiges Rohöl zur Verfügung stand, aus welchem alle durch die Auslandskonkurrenz auf den Markt gebrachten und aus geeigneterem Rohmaterial hergestellten Produkte gewonnen werden mussten.

Die Ueberlegenheit der ausländischen Produkte in Bezug auf Qualität und Preis war es, was die Entwicklung der Oelingdustrie bestimmend beeinflusste und die in verhältnismässig kleineren Betrieben arbeitende, untereinander und mit dem Auslande im heftigen Konkurrenzkampfe stehende Industrie nötigte, durch möglichste Vervollkommnung der technischen Einrichtungen hochwertige Produkte bei möglichst geringen Selbstkosten zu gewinnen.

Zwei Umstande sind es, welche bei der Destillation hiebei berücksichtigt werden mussten: Niedriger Brennmaterialverbrauch und die möglichste Vermeidung von Zusetsungsprodukten. Denn mit dem Grade der Zusetzung bei der Destillation werden die Qualitätsziffern der erhaltenen Produkte, Flammpunkt und Virkosität herabgesetzt, sinkt die Ausbeute und erhöhen sich im gleichen Masse die Gestehungskosten.

Wie diese Aufgabe gelöst wurde und bis zu welcher Vollkommenheit die technischen Einrichtungen zur Destillation der Oele vorgeschritten sind, will ich in kurzen Worten und anhand von Skizzen, Lichtbildern und Modellen erläutern:

Zur Erreichung eines möglichst geringen Brennmaterialverbrauches ist eine möglichst weitgehende kostenlose Vorwärmung des zur Destillation gehenden Rohmaterilas notwendig und hiefür stehen dem Techniker folgende Wärmequellen zur Verfügung: Die in den Destillatgasen enthaltene latente Wärmenge und die Flüssigkeit swärme des von der Destillation abgehenden Rückstandes, die sonst durch das Kühlwasser vernichtet werden.

Diese Wärmequellen werden weitestgehend ausgenützt und zur Vorwärmung des Rohöles in Destillat-Rückstands-Vorwärmern oder kombinierten Vorwärmern benützt.

Fig. I. zeigt schematisch den Gang des Rohöles bei einer aus 10 Destillierblasen, 5 Destillat-Vorwärmern und 2 Rückstandsvorwärmern bestehenden continuierlich arbeitenden Destillationsanlage. Fig. II zeigt schematisch den Gang des Rohöles bei einer diskontinuierlich arbeitenden Destillationsanlage, welche aus einer Destillierblase, einem kombinierten Destillat und Rückstandsvorwärmer und einem nachgeschalteten Rückstandsvorwärmer besteht.

Die durch die Einschaltung solcher Vorwärmer erzielten Ersparnisse sind ganz bedeutende. Sie erstrecken sich nicht nur auf das Brennmaterial, weil in den Vorwärmern bereits die leicht flüchtigen Bestandteile des bis auf 160 Grad C. vorgewärmten Rohöles kostenlos abdestillieren, sie gewähren auch eine namhafte Ersparnis an Kühlwasser und die so ausgestatteten Anlagen lassen sich naturgemäss auch besser forcieren, weil das Rohöl entwässert in die Destillation gelangt. D (Dem im Auftrage der rumänishen Regierung für das rumänische Regierung für das rumänische Contingentierungsgesetz vom Jahre 1908 vom Finanzinspektor Ing. C. Háláceanu verfassten Berichte gemäss verhält sich die Leistungsfähigkeit einer nach Fig. I. ausgerüsteten kontinuierlichen Anlage zu einer ohne jede Vorwarmung arbeitenden kontinuierlichen Destillationsanlage wie 55.2: 35.3, die Leistungsfähigkeit einer nach Fig. II ausgerüsteten discont.

Anlage zu einer ohne jede Vorwärmung arbeitenten diskontinuierlichen Anlage wie 88.2: 48.2).

Während im Vorstehenden auf die Umstände hingewiesen ist, welche die Herabsetzung des Brennstoffverbrauches ermöglichen, sollen nun die technischen Einrichtungen erläutert werden, durch welche eine möglichst zusetzungsfreie Destillation erzielt wird.

Starke Cirkulation des Blaseninhaltes, reichliche Dampfbeschickung während des Destillationsprozesses bei gleichzeitiger Vermeidung eines Ueberdruckes waren bis vor Kurzem in der Rohölindustrie die Gesichtspunkte, von denen man sich bei der Destillation hochsiedender Oele leiten liess und solche in Fig. III dargestellte Destillationsanlagen, welche eigentlich nur ohne Ueberdruck in der Destillierblase arbeiten, da sie mit kaum mehr als 150 cm Wassersäule blos ein rasches Absaugen der enstandenen Zusetzungsprodukte aus den Kondensationsvorrichtungen bewirken sollten, würden allgemein unter dem Namen Vakuumdestillationsanlagen eingeführt.

Die Vorteile, welche die Destillation hochsiedender Oele unter möglichst hohem Vakuum gewährt, waren wohl allgemein bekannt und an Versuchen, derartige Anlagen in der Rohölindustrie einzuführen, hat es nicht gefehlt. (Siehe "das Erdöl IIIBd." v. C. Engler und H. Höfer) Die Schwierigkeiten jedoch, die sich dem Techniker bei Schaffung solcher der Massenfabrikation in der Grossindustrie dienenden Anlagen entgegensetzten, waren bis vor Kurzem unüberbrückbar und der österr. Rohölindustrie gebührt das Verdient Anlagen geschaffen zu haben, welcher dieser Bedingung entsprechens und bei grosser Betriebssicherheit eine ständige, leichte Kontrolle während des Destillationsprozesses gestatten.

Fig. IV. zeigt die schematische Darstellung einer solchen in Oesterreich sich schnell einbürgernden Destillationsanlage für hohes Vakuum (Oesterr. Patent Nro 52202 und Nro 48194) bei welcher mit einem Unterdruck von 69–72 cm Quecksilbersäule, in der Destillierblase gemessen, gearbeitet wird.

Durch die Verlegung der höchsttemperierten Heizgase in das bei Vakuum auf Zug beanspruchte Flammrohr wird eine Ueberhitzung des auf äusseren Druck beanspruchte Kesselmantels verhindert und durch die Verwendung der tiefstehenden Pumpen, welche das kondensierte Oel aus den Kondensationsvorrichtungen absaugen und für den Destillateur sichtbar in den Empfangskasten drücken, ist die stet Kontrolle des Destillationsganges gewährleistet. Diese Anordnung ermöglicht es, alle Apparaturen in eine blos der Konstruktion entsprechenden normalen Höhe über dem Fabriksniveau aufzustellen und es ist blos erforderliche, den barometrischen Kondensator 10 Meter über dem Fabriksniveau zu montieren.

Die bei solchen Anlagen gemachten Erfahrungen sind die allerbesten: Durch die Herabsetzung der Siedetemperatur um 100–120 Gr. C. wird die Menge der Zusetzungsprodukte auf cca ½% reduziert und der Brennmaterialverbrauch auf 3% herabgedrückt, wobei ein Rückstand vom spezifischen Gewichte von 0.91 cca vva 50% hochwertige Oeldestillate ergibt und ein praktisch koksfreier Asphalt von cca 120 Gr. C. Erweichungspunkt entsteht. Bei Destillation des gleichen Materials auf einer Anlage für niedridges Vakuum oder auf einer Krachanlage beträgt der durch die Zersetzung entstehende Destillationsverlust 4%, resp. 8%, der Brennmaterialverbrauch 10%, resp. 20% des Füllinhaltes. In den leiden letzten Fällen sind zu dem die gewonnenen Produkte minderwertiger, der Asphalt ohne entsprechende Nacharbeit nicht marktfähig.

Als bisher unbekannte Tatsache mag noch erwähnt werden, dass, aus den unter Hochvakuum entstehenden Paraffinölen Paraffin von 73° Stockpunkt gewonnen wird.

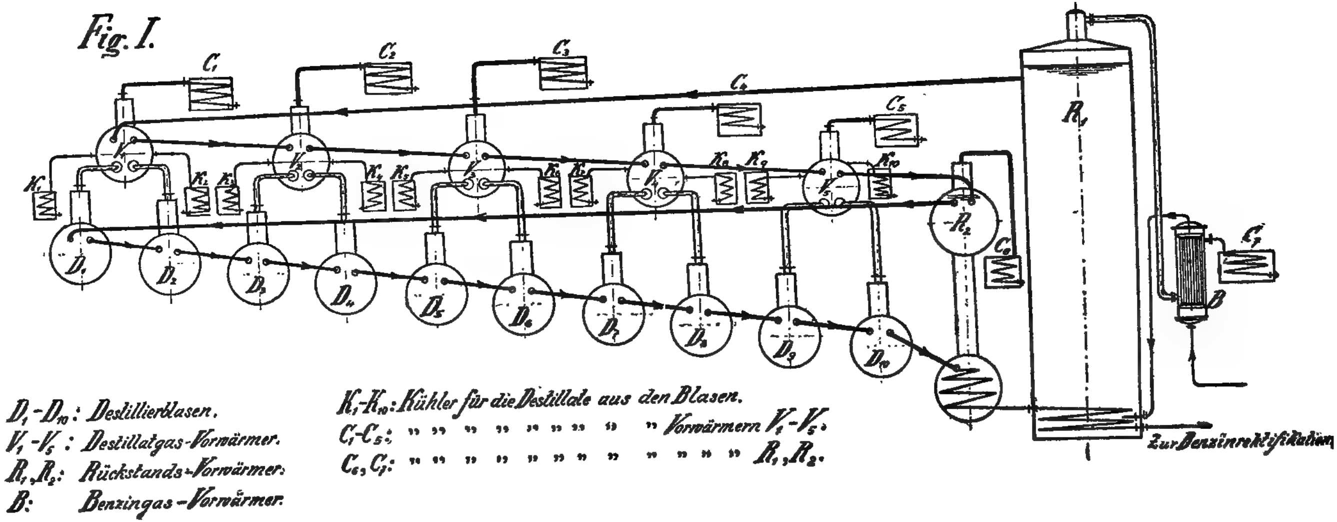
Die Verwendung des Flammrohres bei der Destillier blase und die Anordnung der wegen des besseren Ablassens des Asphaltes an der Unterseite unterbrochenen Innanversteifungsringe, welche sich mit den an der Aussenseite des Kesselmantels befestigten Ringteilen zu geschlossenen Versteifungsringen ergänzen, ermöglichen es Destillationsblasen von verhältnismässig grossem Füllinhalt zu bauen. Ein Füllinhalt von 50 t. ist allgemein gebräuchlich und solche Kessel verarbeiten pro Monat cca 600 Tonnen spezifisch schweren Massut aus Asphalt. Die pro Stunde gelieferte Destillatmenge beträgt hiebei 1700 Liter. Bei einer kontinuierlichen Destillationsarbeit sinkt entsprechend der Brennmaterial verbrauch und steigt die Leistungsfähigkeit einer

Destillierblase im gleichen Verhältnisse wie bei allen Anlagen ohne Vakuum.

Es wird wohl allen Fachleuten leicht fallen, mit Hilfe der hier gemachten Angaben die Vorteile der Verwendung von unter hohem Vakuum arbeitenden Destillationsanlagen für alle speziellen Fälle selbst zu beurteilen.

Die Entparaffinierung der auf tiefstockende Maschinenöle zu verarbeitenden Destillate geschieht in Oesterreich auf den allgemein eingeführten Kristallisatoren Patent "Neumann-Porges," in welchen das langsame Erstarren unter möglichster Ruhe mit Hilfe von gekühlter Salzsohle durchgeführt wird, da anderenfalls die Filtration schwierig, bisweilen unmöglich wird. Die diesbezügliche Erläuterung der weiteren Details würde aber über den Rahmen meines Themas hinausgehen.

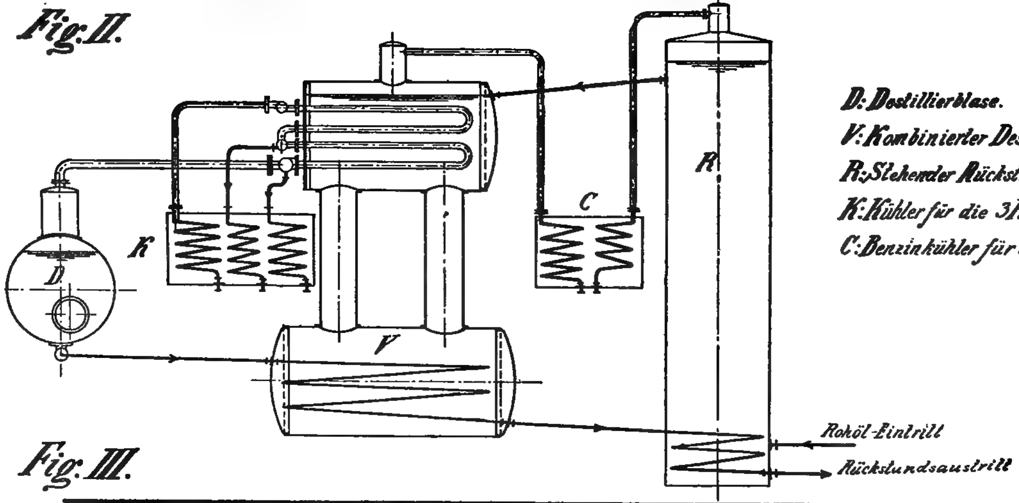
Fig. I.


C₁
C₂
C₃
C₄
C₅
C₆
C₇
V₁
V₂
V₃
V₄
V₅
K₁
K₂
K₃
K₄
K₅
K₆
K₇
K₈
K₉
K₁₀
D₁
D₂
D₃
D₄
D₅
D₆
D₇
D₈
D₉
D₁₀
R₁
R₂
B
Zur Benzinrektifikation
D₁-D₁₀: Destillierblasen.
V₁-V₅: Destillatgas-Vorwärmer.
R₁, R₂: Rückstands-Vorwärmer.
B: Benzingas-Vorwärmer.
K₁-K₁₀: Kühler für die Destillate aus den Blasen.
C₁-C₅: " " " " " " " " " Vorwärmern V₁-V₅.
C₆, C₇: " " " " " " " " " " " " R₁, R₂.

SCHEMA EINER KONTINUIERLICHEN ROHOEL-DESTILLATIONS-ANLAGE AUS 10 DESTILLIERBLASEN, 5 DESTILLAT- UND 2 ROHOELVORWÄRMERN.

SCHEMA EINER DISKONTINUIERLICHEN DESTILLATION MIT VORWÄRMERN.

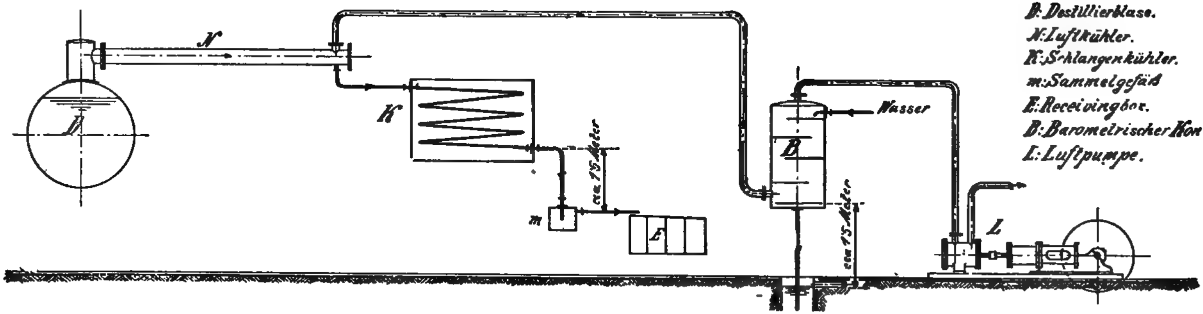
Fig. II.



D: Destillierblase.
V: Kombinierter Destillat- & Rückstandsvorwärmer.
R: Stehender Rückstandsvorwärmer.
K: Kühler für die 3 Fraktionen der Destillierblase.
C: Benzinkühler für die Destillate aus den Vorwärmern.

Fig. III.

SCHEMA EINER DESTILLATION FÜR NIEDRIGES VAKUUM.



D: Destillierblase.
N: Luftkühler.
K: Schlangenkühler.
m: Sammelgefäß
E: Receivingbox.
B: Barometrischer Kondensator.
L: Luftpumpe.

TEMPERATURKURVE

einer kontinuierlichen Destillationsanlage, bestehend aus 6 Petrol-Destillierblasen mit dazugehörigen 6 Vorwärmern, 2 Rückstandsvorwärmern, 6 Oelkesseln ohne Vorwärmer und 4 Hochvakuumblasen bei Destillation von Boryslaver Oel auf Asphalt.

Temperaturen in den Kesseln gemessen.

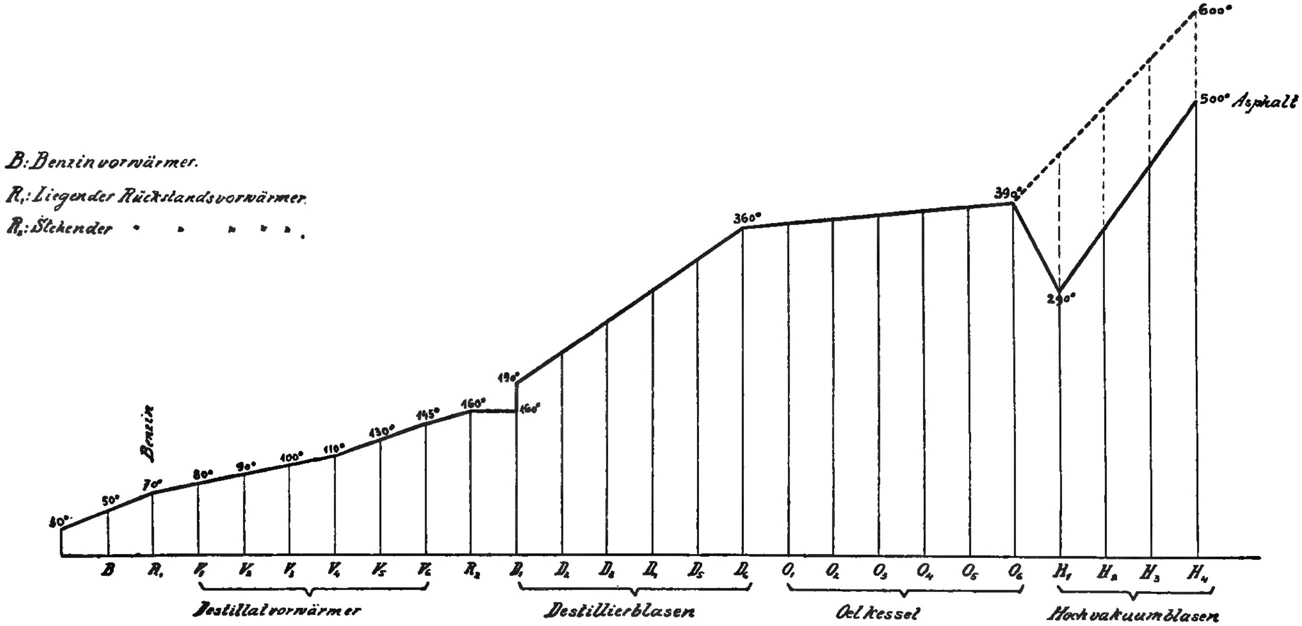
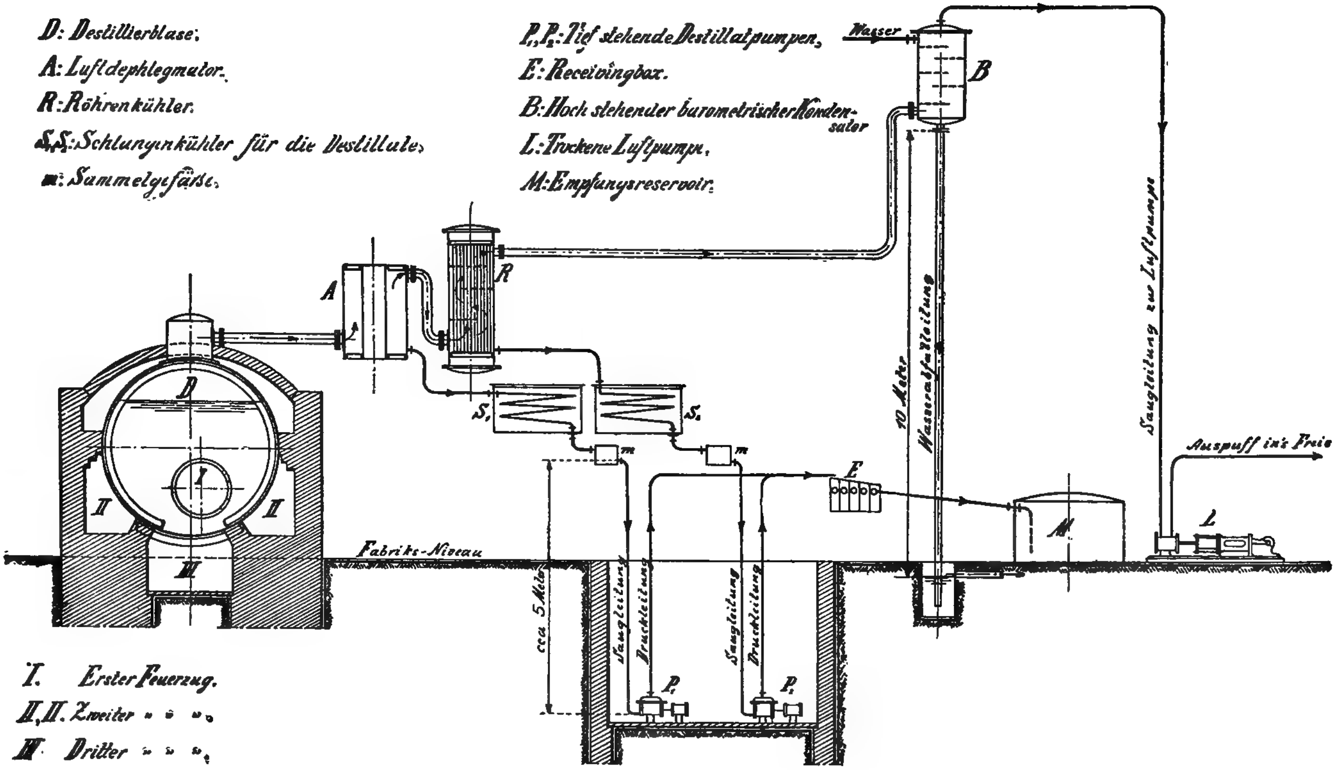


Fig. IV.

SCHEMA EINER DESTILLATION FÜR HOHES VAKUUM.



D: Destillierblase;
A: Luftdephlegmator.
R: Röhrenkühler.
$S_1 S_2$: Schlungenkühler für die Destillate,
m: Sammelgefässe.

$P_1 P_2$: Tief stehende Destillatpumpen,
E: Receivingbox.
B: Hoch stehender barometrischer Kondensator
L: Trockene Luftpumpe.
M: Empfangsreservoir.

I. Erster Feuerzug.
II, II. Zweiter " " ".
III. Dritter " " ".

UEBER DIE VERWENDUNG VON NICHT VORGEWAERMTEN KOKSOFENGAS IM MARTINOFEN

OSCAR TIMMERSBACH
Breslau, Germany

Die deutsche Eisenindustrie hat in den letzten Jahren ihr besonderes Augenmerk darauf gerichtet, die grossen Mengen der Ueberschussgase, welche sich bei den neuen Koksofenkonstruktionen ergaben, ausser zur Krafterzeugung, auch in den huettenmaennsichen Betrieben moeglichst vorteilhaft und gewinnbringend zu verwerten.

Waehrend zunaechst das Koksofengas nur zu Waermzwecken in den Oefen benuetzt wurde, fand die erste erfolgreiche Verwendung von Koksofengas in Siemens-Martin Oefen in Oberschlesien auf der Hubertus-Huette statt, woselbst Direktor Amende seit 1907 Flusseisen mit Koksgas in Mischung mit Generatorgas herstellt.

Im Jahre 1909 ging Direktor Wirtz von der Deutsch-Luxenburgischen Bergwerks & Huetten A. G., in Muehlheim a/d Ruhr dazu ueber, das Koksofengas mit Hochofengas zu mischen und ein Mischgas von rund 2000 Waermeeinheiten zur Stahlfabrikation zu verwenden.

Desgleichen begann Direktor Wirtz im Jahre 1911 damit, einen Martinofen mit vorgewaermten Koksgas allein zu betreiben. Ueber diese aeusserst erfolgreiche Verwendung der Koksofengase in Mischung mit Hochofengas, beziehungsweise allein ohne Zusatz zur Stahlfabrikation, habe ich auf der Hauptversammlung des Vereins Deutscher Eisenhuettenleute in Breslau am 24. Dezember 1911 ausfuehrlich berichtet und auf die Wichtigkeit dieser neuen Verwendungsart der Koksofen- und Hochofengase fuer die Entwickelung der Eisenindustrie hingewiesen,—eine Verwendungsart, die umso schwerer in die Erscheinung tritt, als in Zukunft der Martinofen ohne Zweifel von den Stahlwerken gegenueber dem Converter aus Qualitaetsgruenden bevorzugt werden wird.

Bei den bisherigen Untersuchungen ueber die Verwendung von Koksofengas im Martinofen stellte sich heraus, dass die Vorwaermung des Koksofengases in den Regeneratoren eine Zersetzung des Gases unter gleichzeitiger nicht unwesentlicher Verringerung des Heizwertes zur Folge hatte. Zwar war wohl von der Generatorgasbeheizung der Martinoefen bekannt, dass das Gas in den Kammern zersetzt wird, wie z. B. aus Tabelle I hervorgeht, doch belief sich die Verringerung des Heizwertes nur auf etwa 4%, konnte also vernachlaessigt werden.

Bei der Verwendung von Koksofengas in Mischung mit Hochofengas ergab sich bereits gemaess Tabelle II, eine groessere Zersetzung, so dass eine Heizwertverminderung bis zu 13% vor sich ging.

Untersuchungen endlich mit Koksofengas allein zeigten auf der Friedrich-Wilhelmshuette als Ergebnis, dass Gas mit rund 4500 Calorien bei Erhitzung auf 900° eine Verminderung des Heizwertes von 13% erlitt, bei Erhitzung auf ca. 1000° eine solche von 14% und bei Erhitzung auf 1065° eine Heizwertverminderung von ca. 27% wie die nachstehende Gegenueberstellung (Tabelle III) des naeheren vor Augen fuehrt.

Die Zersetzung beginnt im besonderen schon bei ueber 700°, wie aus den nachstehenden systematischen Untersuchungen von Koksofengas der Friedenshuette in Ober-Schlesien hervorgeht. (Tabelle IV.)

Beim Erhitzen des Koksofengases auf 1000–1060° d.h. auf die in der Martinofenpraxis meist uebliche Gaserhitzungs-Temperature, wurde hier also ebenfalls eine Heizwertabnahme bis rund 24% festgestellt. Die Veraenderung der Gaszusammensetzung im Einzelnen, sowie die Heizwertabnahme insgesamt fuer das Koksofengas und fuer seine einzelnen Bestandteile speziell sind aus den nachstehenden Tabellen V and VI ersichtlich.

Da bei diesen Untersuchungen verschiedene Koksofengase fuer die einzelnen Temperaturen verwendet wurden, sodass ein Vergleich unter einander nicht angaenglich erscheint, wurden weitere Versuche ueber die Zersetzung von Koksgas beim Leiten ueber erhitzten Chamotte mit ein und demselben Gas bei steigender Temperatur angestellt.

Bei der Versuchsreihe in Tabelle VII, blieb der Chamotte, ueber den das Gas geleitet wurde, jeweilig von dem durch Dissociation abgeschiedenen Kohlenstoff bedeckt, waehrend bei der Versuchsreihe in Tabelle VIII der Chamotte nach jedem Versuch mit Sauerstoff ausgebrannt wurde.

Die Heizwertabnahme stellt sich bei rund 800° auf 2–6%, bei 900° auf weitere 6–13%, bei 1000° auf weitere 3–7% bei 1100° auf weitere 2–9% und bei ueber 1200° auf nochmals 14% und insgesamt ergab sich eine Verminderung des Heizwertes bei Erhitzung auf 1200° um ein ganzes Drittel. Schaubild I kennzeichnet diese Temperaturabnahme fuer die einzelnen Temperaturintervalle in anschaulicher Weise.

Im Schaubild II wird noch die Zersetzung des Methans bei einem besonders methanreichen Gas vor Augen gefuehrt, wobei das Gas ebenfalls ueber Chamotte geleitet und letzteres nach jedem Versuch mit Sauerstoff bei 1250° ausgebrannt wurde.

Gas-Analyse.

O_2 = 0,6 Vol. %
CO = 3,2 " "
SKW[1] = 0,6 " "
CH_4 = 57,6 " "
H_2 = 27,2 " "
N_2 = 10,6 " "

Wenn man sich bei den Versuchsreihen I und II in den Tabellen VII und VIII die Veraenderung der Gaszusammensetzung bei der Erhitzung bis 1200° naeher ansieht, so findet man folgendes Bild:

			Versuchsreihe	
			I	II
Vermehrung	des H	um	75%	78%
"	des CO	"	50%	129%
Verminderung	des CH_4	"	77%	83%
"	" CO_2	"	100%	100%
"	" SKW	"	100%	100%

Der Schwerpunkt bei den Reaktionen, die durch die Erhitzung des Koksgases eintreten koennen, ruht bei der Zersetzung der Kohlenwasserstoffe; diese scheiden zunaechst Kohlenstoff ab, welcher sich dann mit O verbindet unter Bildung von CO oder CO_2; ebenso kann er sich aber auch mit CO_2 unter Bildung von CO vereinigen. Des weiteren verbinden sich die CH-Stoffe unter Einwirkung anderer Gase, z.B. wirkt CO_2 auf CH_4 ein. So fand Lang[1] bei einem Gemenge von CH_4 und CO_2:

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[1] Schwere. Kohlenwasserstoff.

	Vor dem Erhitzen:	Nach dem Erhitzen auf 954–1054° C	
I.	33.3% CO_2	26.8% CO_2	6,4% CO
II.	29.4% CO_2	20.1% CO_2	8,2% CO

Die Umsetzung erfolgt nach der Gleichung:

$CH_4 + 3\,CO_2 = 4\,CO + 2\,H_2O$; der Wasserdampf kann sich dann wieder zersetzen nach der Gleichung:

$CO + H_2O = CO_2 + 2\,H$; auch CH_4 kann auf den Wasserdampf einwirken nach der Gleichung:

$$CH_4 + H_2O = CO + 6\,H$$

Jedenfalls erklaert sich die verschiedenartige Gasveraenderung und die verschiedenartige Brennwertverminderung bei der Erwaermung des Koksgases hauptsaechlich durch die verschiedenartige Einwirkung der einzelnen Bestandteile auf einander.

Man geht nach dem Vorstehenden nicht fehl, wenn man in den heutigen Martinoefen bei Benutzung der Gaskammern zur Kohsofengasvorwaermung mit einer *Verringerung des Koksofen-Heizwertes von* $\frac{1}{4}$–$\frac{1}{8}$ *rechnet.*

Will man die Abhitze der Verbrennungshitze wenigstens in etwas durch Vorwaermung des Gases ausnuetzen, so koennte man die Gaskammern verkleinern und das Koksofengas auf 500 bis maximum 700° vorwaermen, da bei 500° eine merkliche Zersetzung und damit Verminderung des Heizwertes des Koksofengases noch nicht eintritt. Wenn man aber bedenkt, dass man durch Vorwaermen des Koksofengases auf 500° nur circa 180 Calorien und durch Vorwaermung auf 700° nur circa 250 Calorien pro cbm Gas gewinnt, d.h. ebensoviel, wie durch die Zersetzung des Koksofengases an Heizwert verloren geht, und andererseits beruecksichtigt, dass die durch Verbrennung von kaltem Koksgas mit erhitzter Luft erzielte Temperatur fuer die Stahlerzeugung ausreicht, so duerfte eine Vorwaermung des Koksofengases selbst auf 5–700° keinen besonderen Vorteil nach sich ziehen.

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[1] Cf. Dichmann "der basische Herdofenprozess," p. 29.

Infolgedessen ist auch die Societe-Cockerill, Belgien in diesem Jahre dazu uebergegangen, Martinoefen mit *kaltem* Koksofengas zu heizen, nachdem sie seit 1909, wie ich in meinem Breslauer Vortrage bereits erwaehnte, in ihrer Stahlgiesserei bei Flammoefen von 4 bezw. 7 t Fassung mit kaltem Koksofengas das nur von einer Seite zugefuehrt wurde, gute Resultate erzielt hat.

Der Martinofen in Seraing hat 12½ t Fassung und ist basisch zugestellt. Nach Mitteilung des Betriebsingenieurs betraegt der Gasverbrauch ca. 300 CBM pro t Stahl; es entspricht dies also so ziemlich den Erfahrungen bei dem gleich grossen Martinofen mit saurer Zustellung auf der Friedrich-Wilhelmshuette mit vorgewaermten Koksofengas. Auch hier wie dort trat eine Productionssteigerung von ca. 15% ein.

Die bisherigen Betriebsresultate beziehen sich auf relativ kleine Martinoefen, jedoch berechtigen sie zu dem Schluss, dass bei grossen Oefen der Verbrauch im Koksofengas pro t Stahl nicht mehr als 225 cbm betragen wird, wahrscheinlich aber nur 200 cbm, besonders mit Ruecksicht darauf, dass der Kohlenverbrauch pro t Stahl von der gleichmaessigen Gaslieferung der Generatoren abhaengt,—eine Bedingung, die bei Koksgasbeheizung gesichert ist. Der geringe Koksgasverbrauch ruehrt vor allem daher, dass die erzielte Flammentemperatur im Martinofen hoeher ist, als bei Generatorgasbeheizung. Wenn in letzterem Falle als hoechst erreichbare Flammentemperatur nur 1788° C gefunden wurden, lassen sich mit Koksofengas Temperaturen von 1850° C und mehr mit Leichtigkeit erzielen. Infolgedessen wird zunaechst weniger Zeit zum Einschmelzen des Schrotts benoetigt, nicht minder aber auch die Zeit fuer das Frischen des Eisens vermindert, indem einerseits im ersten Teile der Charge das Bad besser durchgemischt wird, weil bei der hoeheren Badtemperatur das Bestreben des Kohlenstoffes sich mit Sauerstoff zu verbinden waechst und weil die Waermeuebertragung von der heisseren Flamme auf das Bad wirksamer wird; anderseits aber bleibt zu beruecksichtigen, dass im letzten Teile der Charge, wenn das Bad ruhiger fliesst, eine Waermeuebertragung nur durch Leitung stattfindet, sintemalen die heisseren Teile des Bades leichter sind und daher oben schwimmen, wohingegen die kaelteren Partien unten liegen. Die durch das Koksgas erzielte hoehere Temperatur wirkt daher dann abkuerzend auf die Chargendauer; vor allem aber ist sie von besonderer Wichtigkeit, weil das Bad mit der C–Abscheidung immer schwerer schmelzbar, d.h. also die Waermezufuhr dann umso notwendiger wird.

Die Waermeaufnahmefaehigkeit des Bades ist ferner ueberhaupt waehrend der Chargezeit verschieden, so leicht laesst sich aber die Zusammensetzung des Generatorgases nicht aendern, waehrend man mit Koksgas ohne Anstand leicht regulieren kann, so dass auch hierdurch eine Zeitersparnis und damit eine Erniedrigung des Brennstoffverbrauches erzielt wird, zumal jeder Zeitgewinn auch eine Erniedrigung des Verlustes durch Strahlung und Heizung nach sich zieht.

Was nun im Besonderen die Verwendung von kaltem Koksgas im Vergleich zu der von vorgewaermten Gas anbelangt, so gilt, abgesehen von der durch die Erhitzung eingetretenen Heizwertverminderung bis zu 33%, folgendes:

Im Martinofen soll eine Flamme mit viel strahlender Waerme erzeugt werden, um nicht nur durch directe Beruehrung zu heizen sondern vor allem durch Waermeausstrahlung auf das Bad und die Ofenwandung. Hierzu ist freier C noetig. Bei kaltem Koksofengas entstehen durch die Dissociation der CH-Stoffe viele Teilchen freien Kohlenstoffs, welche sich auf die Flammentemperatur erhitzen und viel Licht und Waerme ausstrahlen, so dass eine bessere Waermeuebertragung auf das Bad erfolgt, zumal der abgeschiedene Kohlenstoff auch in der zweiten Ofenhaelfte fuer eine Flammenbildung mit grosser Waermeausstrahlung Sorge traegt. Es ist dies von wesentlicher Bedeutung, weil bei den modernen Martinoefen bis zu 100 t, wie sie heute in Deutschland mit 12 m Herdlaenge gebaut werden, die Charge natuerlich auf diese grosse Herdlaenge hin gleichmaessig zum Kochen gebracht werden muss.

Die Wasserstoff-Flamme an sich ist kaum sichtbar. Je mehr H, desto kuerzer und heisser die Flamme. Da der H-Gehalt beim vorgewärmten Koksgas durch die Erhitzung bis 75%

zunimmt, so zeigt kaltes Koksgas eine laengere Flamme, die eher bis zum anderen Ende des Ofens reicht, zumal auch mit abnehmender Erhitzung des Gases die Flamme ebenfalls laenger wird.

Bei erhitztem Koksgas entsehen waehrend des Reversierens Gasverluste, indem alles Gas zwischen Herd und Reversier-Ventil nach dem Ventil zurueck muss (Rueckstromverlust) und waehrend des Umsteuerns direkte Verbindung zwischen Esse und Gasleitung vorliegt,—bei kaltem Koksgas fallen diese Verluste fort. Da ferner die fuer die Umkehr der Gase in den kammern und Kanaelen erforderliche Zeit geringer ist, so wird auch im Ofen die Flammenfuehrung nicht so lange aufgehoben und die Flamme schlaegt nicht so lange ungehemmt ans Gewoelbe.

Die Reversierventile sind weiterhin bei den grossen Gasmengen der modernen Martinoefen der schaedlichen Temperatur ausgesetzt, was bei kaltem Koksgas nicht eintritt.

Durch den Fortfall des eigentlichen Gas-Reversierens besteht auch keine Explosionsgefahr mehr, die sonst in den Kammern und Kanaelen in die Erscheinung treten kann.

Baulich ergibt sich ferner eine Verbilligung der Ofenkonstruktion, nebst Verkleinerung der Gasleitungen. Verbilligung der Ventile, sowie eine bessere Armierung und Verankerung des Ofens.

Im Vergleich mit dem Generatorgas kaeme dann noch ausser der nicht unerheblichen Ersparnis an Arbeitsloehnen hinzu, dass keine Staub-und Teerablagerungen in den Leitungen, Kanaelen und Ventilen stattfinden, so dass die hieraus sich ergebenden Betriebsstoerungen fortfallen; desgleichen treten dadurch auch keine Querschnittsveraenderungen in den Gasleitungen ein, wodurch die Ofenleistung erheblich beeintraechtigt wird und der Ofen zuletzt Gefahr lauft, zum Erliegen zu kommen. Die frueher oft gehoerte Befuerchtung, dass bei Koksgasbeheizung das Gewoelbe mehr angegriffen wuerde, als bei Generatorgasbeheizung, trifft nicht zu,—wie die Praxis ergeben hat—es erklaert sich dies dadurch, dass heisse Luft leichter ist als kaltes Koksgas, also erstere mehr das Bestreben hat, nach oben zu steigen, und dadurch dass die bei Koksgasverwendung benoetigte groessere Luftmenge die Flamme besser vom Gewoelbe abhaelt.

Die Qualitaet des Stahles wird ebenfalls durch Verwendung von

Koksgas gefoerdert, weil das Koksgas ein schwefelarmes Gas ist, im Gegensatz zu manchem Generatorgas. Je reiner das Gas, desto weniger Schwefel vermag das Bad aufzunehmen, falls nicht an sich eine Schwefelaufnahme des Stahles aus dem Heizgase durch die basische Schwefeldecke verhindert wird.

Auch hinsichtlich des Wasserstoffgehaltes hat die bisherige Praxis keinen Anhalt dafuer gegeben, weder bei Verwendung von Koksofengas in Mischung mit Hochofengas, noch bei Verwendung von Koksofengas allein, dass die Qualitaet des Stahles irgendwie beeintraechtigt wird.

Diesen Vorteilen steht nun ein Nachteil gegenueber, indem naemlich bei Heizung mit kaltem Kokosgas bei den heutigen Martinoefen-Konstruktionen der Abzug der Verbrennungsgase nur durch die hochliegenden Luftzuege erfolgt und nicht mehr auch durch die direkt ueber dem Bad liegenden Gaszuege.

Es faellt dies besonders bei den grossen Martinoefen ins Gewicht, welche eine Herdlaenge von 10–12 m aufweisen, wobei die Verbrennungsprodukte in der zweiten Haelfte der Herdlaenge durch den Abzug direkt unter dem Gewoelbe durch die hoch liegenden Luftzufuehrungskanaele wesentlich vom Bad abgelenkt werden, sodass dieser Teil des Bades mehr Zeit und Waerme zur Erhitzung und Fertigstellung des Bades benoetigt, als der erste Teil.

Doch laesst sich diesem Uebelstande dadurch abhelfen, wie dies bereits in einer zum Patent angemeldeten Konstruktion geschieht, dass die Einfuerhrung der Verbrennungsluft in den Ofen ausser durch die obligaten oberen Luftzufuehrungskanaele noch durch neben dem Gaszufuehrungskanal vorgesehene Hilfsluftzufuehrungskanaele, welch letztere mit dem ersteren in Verbindung stehen.

Auf diese Weise koennen die Verbrennungsgase in der Abzugsseite durch die unteren Luftzuege ebenfalls entweichen und durch diesen Abzug direkt ueber dem Bade wird die Flamme scharf auf das Bad niedergehalten und nicht vorzeitig von der Charge abgelenkt. Waehrend beim Abzug nur durch die hoch liegenden Luftzuege die Flamme nach der Abzugsseite hin direkt auf das Gewoelbe geleitet wird, worunter dieses natuerlich zu leiden hat.

Durch die gleichzeitige Einrichtung der unteren Luftzuege neben den Gaszuegen wird der Luftstrom auch von den Seiten, nicht nur von oben, eingehuellt, sodass eine innige Mischung von Gas und Luft erfolgt und unmittelbar ueber dem Bade eine kraeftig oxydierende Flamme entsteht, die auf die Chargendauer von wesentlichem Einfluss ist, indem der Einsatz rasch verschmilzt und schnell gefrischt wird.

Von welch' grosser Bedeutung diese innige Mischung von Luft und Gas ist, geht daraus hervor, dass im Martinofen mit vorgewaermten Gas d.h. Gaskammern die Verbrennungsprodukte, welche durch die hoch liegenden Luftzuege entweichen, einen erheblichen Sauerstoffueberschuss aufweisen, wohingegen die durch die tiefer liegenden Gaszuege abziehenden Verbrennungsgase einen Mangel an Sauerstoff zeigen.

Durch die innige Mischung von Gas und Luft findet aber nicht minder sofort eine rasche und relativ vollstaendige Verbrennung statt, sodass die Gase bereits im Ofen vollstaendig verbrennen und nicht unverbrannt in den gegenueberliegenden Ofenkopf abziehen und die Flamme bis weit in die Kammern und sogar in die Reversierventile hineinschlaegt,—eine Gefahr, der sonst die Stirnwaende und Ofenkoepfe auf die Dauer nicht Stand halten koennen.

Waehrend bei Vorwaermung des Heizgases (einerlei ob Koksgas oder Generatorgas) der Treffpunkt von Luft und Gas oberhalb des Bades sich im Laufe der Zeit immer zurueck verschiebt, und der nach der Abzugsseite hin zu beheizende Teil des Herdes immer schwieriger heiss gehalten werden kann, tritt diese Verschiebung des Treffpunktes bei Verwendung von kaltem Koksofengas viel weniger in die Erscheinung infolge der gleichzeitigen parallelen Luftufuehrung neben den Gaszuegen. Infolgedessen arbeitet der Ofen von seiner in Betriebsetzung an stets gleichmaessiger und bleibt stets auf seiner ganzen Laenge, auch nach der Abzugsseite hin, leichter heiss zu halten.

Beim Rueckblick auf vorstehende Ausfuehrungen ergibt sich, dass fuer die Verwendung des Koksofenueberschussgases in Siemens-Martinoefen zweckmaessig zwei Wege in Frage kommen. Entweder ist das Kokosofengas mit Hochofengas zu mischen so zwar, dass das Mischgas den calorischen Wert eines guten Generatorgases erhaelt, und Bau und Betrieb Martinoefen dann in derselben Weise wie bei Generatorgasbeheizung erfolgt—oder aber das Koksofengas wird in kaltem Zustande in den Ofen eingefuehrt unter Vereinfachung der Ofenkonstruktion nebst Leitungen etc. und unter Verbilligung der Arbeitsloehne. In beiden Faellen tritt eine solche Erniedrigung der Stahlerzeugungskosten ein, dass die neue Art der Koksofengasverwendung fuer die Eisenindustrie eine aeusserst wichtige Umwaelzung bedeutet, eine Umwaelzung, die es ihr ermoeglicht, vom Roheisen bis zum Walzwerksfertigfabrikat ohne weiteren Kohlenverbrauch auszukommen.—

TABELLE I

GENERASORGAS-ANALYSEN

(Nach Prof. Mayer "Wärmetechnik des Martinofens" p. 73.)

	Gas—vor dem Eintritt in die Gaskammer		Gas—nach dem Erhitzen in den Gaskammer	
CO_2	6.3	Vol %	5.9	Vol %
S.K.W.	0.3	“	0.15	“
O_2	0.2	“	.....	“
CO	22.7	“	23.7	“
CH_4	2.6	“	0.9	“
H_2	13.4	“	16.1	“
N_2	54.5	“	53.25	“
	100.0	%	100.00	%

Tabelle II.

	Hochofengas			Koksofengas			Mischgas am Ventil			Mischgas vorgewärmt		
	Vol.%	gr %	1cbm:gr	Vol%	gr %	1cbm:gr	Vol%	gr %	1cbm:gr	Vol%	gr %	1cbm:gr
CO_2	10.6	16.25	209	2.4	9.48	47.3	3.2	6.97	63	3.4	7.69	66.9
S.K.W.	-	-	-	1.8	6.14	30.6	1.6	3.00	27.2	0.4	0.79	6.8
CO	29.4	28.58	367.5	4.6	11.55	57.5	16.8	23.29	210	15.8	22.8	197.5
H_2	3.0	0.002	0.27	55.1	9.91	49.6	28.6	2.81	25.7	32.2	3.42	29.0
CH_4	-	-	-	25.5	36.3	181.0	8.6	6.71	61.0	6.4	5.2	45.5
N_2	57.0	55.16	712.5	10.6	26.62	132.5	41.2	57.22	515	41.8	60.10	552.5
	100	100	1289	100	100	498.5	100	100	902	100	100	901.2
WE	899			4266			2213			1910		

III

Tabelle

Koksofengas-Analysen

I.

Gas vor dem Eintritt in die Gaskammer		Dasselbe Gas beim Austritt aus der Kammer nach Erhitzung auf c. 900°	
CO_2 =	3.4%	CO_2 =	2.8%
CO =	5.6%	CO =	6.0%
H_2 =	47.7%	H_2 =	43.5%
CH_4 =	30.3%	CH_4 =	25.3%
	4560 W.E.		3950 W.E.

Heizwertabnahme - 13%

II.

Gas vor dem Eintritt in die Gaskammer		Dasselbe Gas beim Austritt aus der Kammer nach Erhitzung auf c. 1000°	
CO_2	2.8%	CO_2 =	3.8%
CO	7.4%	CO =	8.4%
H_2 =	44.7%	H_2 =	43.6%
CH_4 =	29.9%	CH_4 =	23.3%
	4450 W.E		3820 W.E

Heizwertabnahme - c. 14%

III.

Gas vor dem Eintritt in die Gaskammer		Dasselbe Gas beim Austritt aus der Kammer nach Erhitzung auf 1065°	
CO_2 =	2.4%	CO_2	3.2%
S.K.W. =	2.0%	S.K.W. =	0.2%
CO =	4.2%	CO =	9.6%
H_2 =	51.1%	H_2 =	35.7%
CH_4. =	30.2%	CH_4 =	20.5%
	4580 W.E.		3400 W.E.

Heizwertabnahme - c 26%

IV.

Gas vor dem Eintritt in die Gaskammer		Dasselbe Gas beim Austritt aus der Kammer nach Erhitzung auf 1065°	
CO_2	2.6%	CO_2 =	2.6%
S.K.W	2.0%	S.K.W. =	0.6%
CO	5.0%	CO =	8.8%
H_2	49.9%	H_2 =	35.2%
CH_4	30.1%	CH_4 =	18.7%
	4560 W.E.		3300 W.E

Heizwertabnahme - c. 28%

Tabelle IV

Koksofengas-Analysen

Vordem Erhitzen.

Nº		Vol. %	Vol. %	Vol. %	Vol. %	Vol. %	Vol. %	Vol. %
		CO_2	S.K.W.	O	CO	H	CH_4	N
1		5.0	1.6	0.6	10.8	49.2	21.3	11.5
2		5.0	1.4	0.4	11.2	43.8	24.6	13.6
3		4.4	0.8	1.2	11.4	54.7	16.4	11.1
4		4.0	1.4	1.2	11.4	54.8	16.4	10.8
5		5.2	1.4	1.0	11.0	48.8	19.5	13.1
6		5.6	1.4	0.6	10.0	45.0	19.8	17.6

Nach dem Erhitzen.

Nº	Erhitzungstemperatur: °C	Vol. %	Vol. %	Vol. %	Vol. %	Vol. %	Vol. %	Vol. %
		CO_2	S.K.W.	O	CO	H	CH_4	N
1	750-760	4.0	0.8	0.6	12.6	50.2	20.5	11.3
2	800	3.0	0.3	0.4	13.3	45.2	23.2	14.6
3	900-940	3.0	0	0	14.8	58.6	11.4	12.2
4	900-940	1.6	0	0	20.0	58.5	7.8	12.1
5	1000-1040	1.2	0	0	19.8	52.6	12.6	13.8
6	1000-1060	0.4	0	0	19.2	60.0	4.8	15.6

Tabelle. V

Veränderung der Gaszusammensetzung im Einzelnen.

Nº	CO_2. Veränderung.		C_2H_4. Veränderung.		O. Veränderung		CO. Veränderung.		H. Veränderung.		CH_4. Veränderung.		N. Veränderung.	
	absolut	in %	absolut	in %	absolut	in %	absolut	in %	absolut	in %	absolut	in %	absolut	in %.
1.	-1	-20.0	-0.8	-50.0	±0	0	+1.8	+16.65	+1.0	+2.04	-0.8	-3.75	-0.2	-1.76
2.	-2	-40.0	-1.1	-78.5	±0	0	+2.1	+18.75	+1.4	+3.19	-1.4	-5.7	+1.0	+7.35
3.	-1.4	-31.8	-0.8	-100.0	-1.2	-100.0	+3.4	+29.8	+3.9	+7.14	-5.0	-30.5	+1.1	+9.9
4.	-2.4	-60.0	-1.4	-100.0	-1.2	-100.0	+8.6	+75.5	+3.7	+6.78	-8.6	-52.4	+1.3	+12.04
5.	-4.0	-77.0	-1.4	-100.0	-1.0	-100.0	+7.8	+70.9	+3.8	+7.78	-6.9	-35.4	+0.7	+5.32
6.	-5.2	-93.0	-1.4	-100.0	-0.6	-100.0	+9.2	+92.0	+15.0	+33.33	-15.0	-75.6	-2.0	-11.33

Tabelle VI

Heizwert vor dem Erhitzen

1 Cbm.

Nº		W.E. gebende Bestandteile des Gases					Heizwert des Koksofen gases	
		CH_4	CO	H_2	C_2H_4			
		W.E.	W.E.	W.E.	W.E.			WE
1		1837 ~~2029~~	330 ~~328~~	1272 ~~1502~~	227 ~~238~~		3666	~~4097~~
2		2129 ~~2344~~	343 ~~340~~	1134 ~~1337~~	193 ~~209~~		3799	~~4230~~
3		1413 ~~1562~~	349 ~~346~~	1416 ~~1669~~	113 ~~119~~		3291	~~3696~~
4		1413 ~~1562~~	349 ~~346~~	1420 ~~1672~~	199 ~~209~~		3381	~~3789~~
5		1680 ~~1858~~	337 ~~334~~	1263 ~~1489~~	199 ~~209~~		3479	~~3890~~
6		1708 ~~1886~~	306 ~~303~~	1165 ~~1373~~	199 ~~209~~		3378	~~3771~~

Heizwert nach dem Erhitzen

Nº	Erhitzungs temperture °C	W.E. gebende Bestandt. d. Gases.				Heiz. Koksofen gases.	Heizwert abnahme.	
		CH_4	CO	H_2	C_2H_4		Absolut	%
		W.E.	W.E.	W.E.	W.E.	W.E.	W.E.	
1	750 - 760	1766	385	1300	113	3564	102	28%
2	800	2000	407	1172	43	3682	177	4.67%
3	900 - 940	985	453	1517		2945	346	10.8%
4	900 - 940	673	612	1513		2798	583	17.2%
5	1000 - 1040	1087	607	1362		3056	423	12.15%
6	1000 - 1060	414	588	1582		2584	794	23.6%

Tabelle. VII

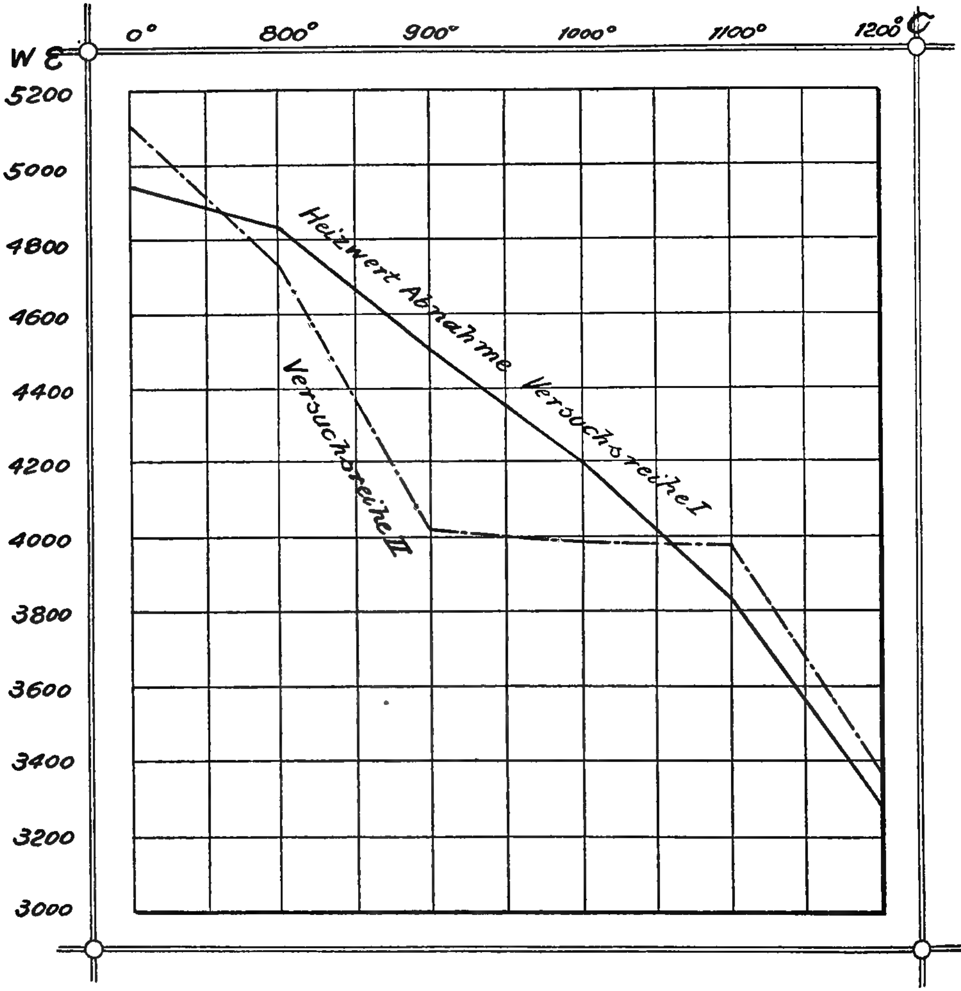
Gas Zusammensetzung vor dem Erhitzen. Vol. %.	Temperatur °C	810	900	1010	1100	1210
	Dauer der Einwirkung in Sekunden	22	18	14	14	16
3.4	CO_2	2.6	2.5	1.1	0.6	0.0
0.7	O_2	0 5	0.4	0.3	0.2	0.0
7.9	CO	8.1	8.7	9.0	11.2	11.8
2.6	S.K.W.	2.2	0.8	0.2	0.0	0.0
31.7	CH_4	28.9	25.1	24.8	16.0	6.8
42.8	H_2	49.3	54.6	57.1	65.1	74.9

VIII

Tabelle.

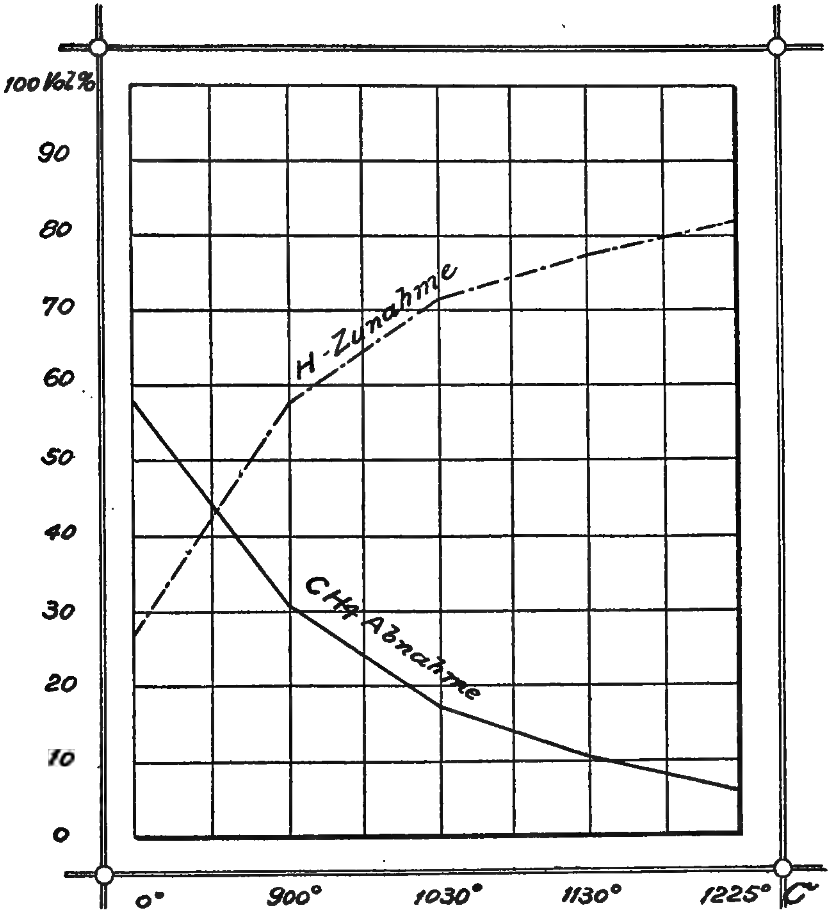
Gas Zusammensetzung vor dem Erhitzen. Vol. %	Temperatur °C	800	900	1000	1100	1220
	Dauer des Erhitzens in Sekunden	14	11	12	13	14
3.4	CO_2	2.1	1.3	1.0	0.7	0.2
0.9	O_2	0.5	0.3	0.2	0.2	0.1
6.3	CO	11.0	12.0	12.9	13.5	14.4
2.7	S.K.W.	2.0	0.2	0.1	0.0	0.0
33.2	CH_4	27.6	20.2	17.3	15.6	5.5
42.6	H_2	48.6	58.8	63.7	66.1	75.7

Schaubild I



0°
800°
900°
1000°
1100°
1200° C
W E
5200
5000
4800
4600
4400
4200
4000
3800
3600
3400
3200
3000
Heizwert Abnahme Versuchsreihe I
Versuchsreihe II

Schaubild II



(*Abstract*)

THE ANALYSIS OF WATER GAS PURIFICATION MATERIAL

E. C. Uhlig,
Brooklyn, N. Y.

This research was undertaken to ascertain the comparative value of the methods published for the analysis of this material, and to obtain a method which would give reasonably accurate results in the shortest time.

Material when received is saturated with water and tarry matter and has to be dried before grinding. 100 grams are placed in a water-jacketed oven at 90° to 95° C., until dry enough for grinding. It is unsafe to hasten the drying as some sulphur may be volatilized. The sample is then ground in a mill as fine as possible.

The methods of analysis tried were all based on oxidation of the sulphur and subsequent precipitation as barium sulphate. The methods differed in the manner in which the oxidation was effected. The barium chloride solution for precipitation was added one c. c. at a time from a burette to the boiling solution to be precipitated; the boiling continued 10 minutes and the solution allowed to stand over night. Where iron was present the barium sulphate was washed with hot 5% HCl, it being found that the barium sulphate was liable to be contaminated with Fe when this washing was omitted.

The methods employed were:

1. Aqua regia method, as used in iron analysis.
2. Fuming nitric acid method.
3. Sodium hydroxide method. Digestion with sodium hydroxide, oxidation with potassium permanganate, and solution in hydrochloric acid.
4. Fusion with sodium carbonate and sodium nitrate.

5. Eschka's method, or heating with powdered magnesite and sodium carbonate.
6. Combustion in a calorimeter bomb with potassium chlorate and sodium peroxide.
7. Graefe's method; combustion in a bottle of oxygen.
8. Extraction with carbon disulphide.
9. Lunge's method; combustion in a current of moist oxygen.

RESULTS OF THE ANALYSES

Oxide Sample No. 1 was tested by methods 1, 3, 4, 5, 6, and 7. The results were all quite close except 5, which were low, owing probably to some sulphur escaping. This was not investigated as the method would not do where many determinations had to be done.

Methods 3 and 4 were accurate but too troublesome for routine work.

Methods 6 and 7 were very suitable for routine work.

Method 1 is accurate but consumes much time. An attempt was made to omit the evaporation to dryness, but the results were high due to silica.

Oxide sample No. 2 was tested by the following methods; 2, 7, 8, and 9.

Methods 2 and 7 gave practically the same results. 8 is very slow and 9 very rapid. These last two methods were not suitable as only the free sulphur was determined, and to properly watch the work of the oxide the total sulphur must be determined.

The bomb method gives accurate results in the least time, but the initial cost of apparatus is high. Graefe's method is accurate and the apparatus not costly, the time is however longer than the bomb method. In the Graefe method solution of the products of combustion in water is all that is necessary. When the insoluble part was treated with hydrochloric acid no sulphur was found. The sulphur in the residue may be disregarded. Sulphur was also determined in the material before use in purification; the results with fuming nitric acid and Graefe's method were found to be nearly the same.

As the gravimetric method is long, a rapid method as desirable.

This was found in the use of the Jackson Turbidimeter, the method being as follows:

To the solution and washings from the Graefe method a drop of phenolphthalein was added, the solution nearly neutralized with 50% HCl and boiled to expel carbon dioxide, filtered into a 500 c. c. flask and washed with cold water. The flask was cooled under a tap, the contents diluted to the mark and well mixed. 10 c. c. were taken with a pipette, run into a 100 c. c. Nessler jar, diluted to 75 c. c. with cold water, a drop of methyl orange added and sufficient N_2 HCl to make slightly acid. A barium chloride, 1 gram, tablet added, the solution diluted to the mark and set aside with occasional shaking until tablet was dissolved. The solution was then poured into the turbidimetric tube and the height on the tube where the candle flame became obscured noted. The average of five readings was taken. From the tables the milligrams of sulphur per 100 c. c. was obtained and the per cent. calculated. Comparison of turbidimeter with gravimetric methods on seven different oxides gave results differing from 0.17 to 0.75%, which is sufficiently accurate for gas works purposes.

When the boiling off of the carbon dioxide was omitted the results were over 2% higher than with gravimetric method.

(*Abstract*)

THE DETERMINATION OF TARRY MATTER IN WATER GAS PURIFICATION MATERIAL

E. C. Uhlig
Brooklyn, N. Y.

Two methods were used, viz.—

I. 10 grams were extracted in a weighed cartridge with carbon disulphide. The loss was tar plus soluble sulphur. The sulphur remained in the sample was then determined and subtracted from the total sulphur previously found. This gave the sulphur extracted. The loss of the cartridge and material on extraction minus the last result above gave the tarry matter.

II. 2 grams were wrapped in an 11 c. m. filter paper and extracted with carbon disulphide. The gain in weight of the flask after expelling the solvent was tar plus soluble sulphur. The contents of the flask were oxidized by fuming nitric acid and the sulphur determined. This subtracted from the previous weight gave the weight of tarry matter.

The second method consumes less time than the first. In both methods it is necessary to tightly enclose the material so that none of the woody portion would float in the solvent and pass into the flask. The extraction and determination of sulphur takes time, and it was thought that a solvent could be obtained which would remove the tar and leave the sulphur behind.

The following solvents were tried: carbon tetrachloride, toluol, petroleum ether, acetone, and ether. A qualitative test of the solubility of sulphur in each was tried, and it was found that sulphur was partly soluble in all. The method for removing tar without at the same time removing sulphur was therefore a failure, and resolved itself into a search for a solvent which would take the place of carbon disulphide which is somewhat dangerous to use on account of inflammability. All the solvents above were tried as a matter of interest. It was found that petroleum ether, aceton, and ether would not answer because their solvent action was incomplete. Carbon disulphide, carbon tetrachloride, and toluol were very good solvents. The latter was slower than the two former. Carbon tetrachloride was very good but slower than carbon disulphide. The latter is the best solvent, with precautions the danger resulting from its inflammability may be avoided.

It is difficult to know when the end of the extration is reached. Extractions were tried where one solvent followed another when the extraction was apparently complete. It was found that the second solvent extracted some more of the material.

Carbon disulphide is the best solvent, being 50% shorter in time than carbon tetrachloride. Either may be used for Works control. Sulphur in purification material evidently exists in three forms:

1. In combination with iron,
2. In combination with tarry matter, and
3. Uncombined or possibly dissolved in the tarry matter.

THE RAPID DETERMINATION OF ASH IN COAL

H. M. Ullmann and N. W. Buch

In a previous publication[1] we outlined methods for the rapid determination of ash and phosphorus in coke, and, as there given, the methods have continued to yield us and others rapid, certain and accurate results. The fundamental idea in determination of ash was, to spread the coke in a thin layer over a weighed platinum dish by means of alcohol, to burn off the alcohol, and then to heat the coke in the brush flame of a blast lamp so that a return eddy of hot gases of combustion might carry with them a supply of preheated air. Five or ten-gram samples were readily incinerated in twenty minutes, and one-gram samples may be burned to ash in a platinum capsule in ten minutes. Continuing with this ash after weighing, it was used for the estimation of phosphorus by treating it with a mixture of nitric and hydrofluoric acids, evaporating rapidly to a small volume, filtering, and then precipitating with molybdate solution and concluding the analysis by the well-known alkalimetric method. Combined results for ash and phosphorus may be arrived at within fifty minutes, and are uniformly accurate.

Anthracite coals of Pennsylvania have always yielded excellent results by the method just described for coke. In dealing with softer coals high in moisture and volatile matter, we have succeeded in adapting the method by observing caution in the initial heating, and by adding an alcohol solution of shellac to prevent the flaking of the coal from the sides of the platinum dish.

In detail the method for highly bituminous and moist coals is as follows,—Five grams of the finely ground coal are put into a previously weighed platinum dish of the usual rounded-bottom shape, of about 150 cc. capacity, or about 9 cm. across the top. The dish is placed on a platinum triangle and heated for about eight minutes at one side with a low flame of a Teclu or Bunsen burner to drive off moisture. The flame is now raised to a height of about 4 cm., placed under the dish and the greater part of the volatile matter is driven off in 2 to 4 minutes. By floating on the surface of water the dish is rapidly cooled, whereupon the semi-coked mass is broken up with a pestle. This can usually be carried out in the platinum dish by gentle pressure; in the case of some hard-coking coals, the mass is ground in an agate mortar and returned to the dish. Four to six cc. of a one-percent alcohol solution of shellac are added, and allowed to steep into the semi-coked coal for a moment. By lateral shaking the whole mass is made uniformly wet, and then by tilting the dish and giving it a slow rotary motion the pasty mass is made to flow well up onto the sides of the dish. With proper manipulation, the coked mass is spread in an even layer over sides and bottom of the dish, and sets in that position due to the slow evaporation of the alcohol. This evaporation may be hastened by blowing on the mass.

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[1] The Chemical Engineer, October, 1909.

Without waiting for the mass to become absolutely dry, or even for all flow to cease, the dish is placed on a platinum triangle and the residual alcohol burned off by applying the small flame of a burner at the top of the dish. As soon as all alcohol has burned off, the dish is heated to bright redness over the full brush flame of a blast lamp, or, better, over two Teclu or Bunsen burners inclined at the proper angle to heat the whole dish. If the coal flakes from the side of the dish before it is burned to ash, it should be cooled and again spread with shellac solution; however, proper first coking should obviate the necessity of this step.

The whole operation of determining the ash requires not more than twenty, or, in rare cases, a maximum of thirty minutes. Weighings for a sample of five-grams may be made within one-half milligram, involving an error at most of .01 percent in the result. Modifications of the above method will suggest themselves as the type of coal approaches anthracite coals. A sample of coal or coke when spread as above and then placed in a muffle does not burn rapidly.

Many private analyses have checked perfectly with slower methods, and we are indebted to the Bureau of Mines of the United States for the following series of samples of varied coals.

The results of the Bureau were kindly checked by Mr. A. C. Fieldner, Assistant Chemist of the Bureau.

No.	State	Ullmann and Buch	Bureau of Mines	Type of Coal
1	W. Virginia	11.49	11.31	Semi-bituminous
2	Colorado	11.79	11.79	Bituminous
3	Pennsylvania	6.29	6.43	Semi-bituminous
4	Pennsylvania	9.09	9.20	Bituminous
5	Colorado	6.89	7.00	Sub-bituminous
6	Alabama	11.03	11.15	Bituminous
7	Pennsylvania	11.63	11.73	Anthracite
8	Wyoming	4.03	4.11	Sub-bituminous
9	Kentucky	3.00	2.99	Bituminous
10	Oklahoma	4.03	4.11	Bituminous
11	Pennsylvania	7.00	6.98	Anthracite
12	Japan	4.32	4.27	Bituminous
13	Washington	10.49	10.54	Bituminous
14	Missouri	8.67	8.55	Bituminous
15	West Virginia	6.12	6.11	Bituminous
16	Montana	6.39	6.48	Lignite
17	Illinois	10.59	10.68	Bituminous
18	North Dakota	9.42	9.59	Lignite

We acknowledge with gratitude the assistance rendered by A. A. Diefenderfer and J. S. Long in the development of the above method.

(*Abstract*)

RESINS IN PALEOZOIC COALS

David White
Washington, D. C.

Resins are found in practically all the lignites and subbituminous coals in which search has been made, lumps (wound or exudate) of typical "rosin" or amber aspect being nearly always present. The amounts originally contributed to the mother peat vary according to the period and region, but the quantity present is largely governed by the varying extent of the decay of the ingredient plant material, since the decay of the accompanying plant tissues effects important concentrations of the resins, which are among the substances most resistant to subaqueous decay. Thus, according to the conditions of deposition, the resins are more concentrated in certain layers and coals.

In the more advanced coals, including the lowest ranks of the so-called bituminous (humic) coals of the later geological epochs resins are similarly present, though the lumps are often deformed and squeezed along bedding planes and into the joints of the coals. In coals of still higher rank the lump resins are found to undergo alteration and reduction, becoming smoky-brown; crackled; dark brown-black, shriveled, and opaque; and appearing finally to be reduced (carbonized) to a black, granular, coaly scale or film. The alteration and reduction of the lump resins (and presumably the microscopical or internal segregations as well) seem to take place while the coals are advanced by the dynamo-chemical processes from the 59 per cent to the 64 per cent fixed carbon ("pure coal" basis) rank. The period in the progress of coalification thus roughly defined seems therefore to compass the reduction and loss from visual recognition of the megascopic resins observed. It also is, in general, coincident with the development, other things being equal, of the standard coking quality in the coals, which thereafter persists until the coals approximate the semianthracite rank.

Resin lumps occur also in some of the coals having less than 60 per cent fixed carbon ("pure coal") in the Paleozoic coal measures of the Mississippi Valley. Many of the carbonized woods in the coals of that region contain needlelike canal fillings referred, on the evidence presented, to the resins. Other very unique material from the Carboniferous of Montana is described, in which the long, threadlike canal fillings, both freed by decay and in place in the coaly residues, are so preserved that they may easily be removed for microscopical or chemical examinations. Though doubtless somewhat changed from their original composition these very remarkable secretions furnish both optical and chemical evidence of their resinous nature.

The conclusion is reached that many of the Carboniferous types of plants were resin-bearing, and that resins were probably as abundant in the Paleozoic coals as in those of the later eras.

DIE BESTIMMUNG DES SEIFENGEHALTS KONSISTENTER FETTE

PROFESSOR DR. J. MARCUSSON
Mitteilung aus dem Königlichen Materialprüfung samt Berlin-Lichterfelde W.

Der Seifengehalt konsistenter Fette wird in der Regel titrimetrisch durch Ermittlung der freien Säure einerseits, der nach Zersetzen der Seifen mit Mineralsäure und Auswaschen der letzteren mit Wasser erhältlichen Gesamtsäure (Summe von freier und aus Seifen in Freiheit gesetzter Säure) andrerseits festgestellt. Die Differenz ergibt die Menge der in Form von Seifen vorliegenden Fettsäuren. Bestimmt man nun noch das Molekulargewicht der Fettsäuren und die Art der Seifenbasis, so lässt sich der Seifengehalt des Fettes berechnen.

Schwierigkeiten können sich bei der Anwendung des titrimetrischen Verfahrens ergeden, wenn dunkle oder künstlich gefärbte Fette zur Untersuchung vorliegen, weil die Titration der dann erhältlichen gefärbten Lösungen manchmal nicht scharf durchzuführen ist.

Ferner ist das Verfahren dann nicht ohne weiteres anwendbar,[1] wenn Seifen wasserlöslicher Fettsäuren zugegen sind, weil diese Säuren bei dem vorgeschriebenen Ausziehen der zur Zersetzung der Seifen verwendeten Mineralsäure mit Wasser gleichfalls z. T. ausgelaugt werden, so, dass der Seifengehalt zu niedrig gefunden wird.

Allgemein anwendbur ist dagegen das nachfolgend beschriebene gewichtsanalytische Verfahren, welches auf der Beobachtung beruht, dass sich die in konsistenten Fetten findenden Seifen durch ihre Schwerlöslichkeit in Aceton von den öligen Bestandteilen und durch ihre leichte Löslichkeit in Benzolalkohol von den in Aceton unlöslichen, rein anorganischen Anteilen trennen lassen.

Versuchsausführung: 10 g Fett werden in einem Erlenmeyer-kölbchen mit 100 ccm frisch destilliertem Aceton in der Kälte solange unter mehrfachem Zerdrücken mit einem vorn abgeplatteten Glasstabe digeriert, bis sich nach einigen Stunden, nötigenfalls Stehen über Nacht, die festen Bestandteile in feiner Verteilung abgeschieden haben. Man filtriert dann ab und wäscht noch so lange mit Aceton aus, bis eine Probe des Auszugs beim Verdampfen keinen nennenswerten Rückstand mehr ergibt. In die Acetonlösung gehen Mineralöle, fette Oele, Teeröle usw. über, ungelöst bleiben auf dem Filter zurück die Seifen (Kalk-Natronseifen usw.) und rein anorganische Bestandteile (Beschwerungsmittel, Kalk, Graphit) Behufs Isolierung der Seifen wird das Filter durchstossen, der Niederschlag mit heissem Benzol-Alkohol (9:1) quantitativ in ein Kölbchen gespült und in diesem mit dem Lösungsmittel kurze Zeit gekocht. Die Seifen gehen in Lösung und können durch Filtration in der Wärme leicht von den Beschwerungsmitteln befreit werden. Die Lösung wird eingedampft, der Rückstand bis zum konstanten Gewicht bei 105° getrocknet. Man erhält so unmittelbar den Gehalt an Seifen.

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[1] Siehe *Holde* Mineralöle und Fette 1909 S. 106.

Bei Gegenwart grosser Mengen Alkaliseife empfiehltes sich, zur schnellen Erreichung des konstanten Gewichtes, die Benzolalkohollösung in einer Schale einzudampfen, welche zuvor mit ausgeglühtem Sand gewogen ist (entsprechend dem Vorgehen bei der Bestimmung der Trokkensubstanz in Seifen). In einzelnen Föllen wurde beobachtet, dass sich die Seifen bei der angegebenen Aceton behandlung nicht in feiner Verteilung ausscheiden, man erhielt vielmehr klumpige, Oel einschliessende Massen. Dieser Missstand war darauf zurückzuführen, dass zur Herstellung der Fette ungewöhnlich zähflüssige und daher in Aceton schwerlösliche Oele verwendet waren. Bei Vorliegen derartig bereiteter Fette giesst man die zuerst erhaltene Acetonlösung ab und behandelt den klumpigen Rückstand von neuem mit 50–100 ccm Aceton. Die Seife scheidet sich dann ölfrei in der erforderlichen feinen Verteilung ab.

Mit Hilfe des Acetonverfahrens lässt sich auch leicht feststellen, ob in einem konsistenten Fett Alkaliseife oder Kalk-bezw. Aluminiumseife enthalten ist. In ersterem Falle löst sich die abgeschiedene Seife beim Erwärmen mit 50% igem Alkohol leicht auf, in letzterem bleibt sie ungelöst. Dieses Verhalten kann auch zur quantitativen Bestimmung von Alkaliseife neben Kalk—oder Tonerde—seife verwendet werden. Man kocht in diesem Falle zweckmässig die acetonunlöslichen Anteile zunächst mit 50% igem Alkohol zum Herauslösen der Alkaliseife, der Rückstand wird dann erst mit Benzolalkohol zur Trennung der Kalkseife usw. vom rein Anorganischen erhitzt.

In Frage gestellt ist die Anwendbarkeit des Acetonverfahrens, wenn pechartige Destillationsrückstände zur Herstellung eines Schmiermittels verwendet sind, weil sich die Pechteile in Aceton nur teilsweise lösen, dagegen ebenso wie Seifen in Benzol-Alkohol übergehen. Solche Schmiermittel sind aber sehr minderwertig und kommen selten vor.

Die nach dem Acetonverfahren erhältlichen Werte liegen in einzelnen Fällen etwas höher als die nach dem titrimetrischen Verfahren gewonnenen. Das ist vielleicht so zu erklären, dass die zur Herstellung konsistenter Fette verwendeten fetten Oele bisweilen merkliche Mengen wasserlöslicher Fettsäuren enthalten, welche sich der titrimetrischen Bestimmung entziehen, bei dem gewichtsanalytischen Verfahren aber infolge der Schwerlöslichkeit der Kalksalze dieser Säuren in Aceton mit zur Wägung gelangen. Die nach den beiden Verfahren bei Vergleichsbestimmungen unter Verwendung heller normal zusammengesetzter Fette erhaltenen Werte sind in nachfolgender Tabelle zusammengestellt.

Gegen die Zuverlässigkeit des Acetonverfahrens könnte angeführt werden, die in Frage kommenden Seifen seien in Aceton nicht unlöslich, sondern nur sehr schwer löslich, der Seifengehalt müsse also zu niedrig gefunden werden. Eine Prüfung dieser Frage hat folgendes ergeben: Beim Abdampfen der Acetonlösung einiger normal zusammengesetzter konsistenter Fette hinterblieben leichtfliessende hellgefärbte Oele, deren Konsistenz in keiner Weise auf Gegenwart nennenswerter Mengen Seife schliessen liess. Der Aschengehalt des Oeles war gleich Null, oder er betrug nur wenige Milligramme, so dass es sich in der Mehrzahl der Fälle erübrigen wird, eine Korrektur für die in Lösung gegangenen Seifen anzubringen. Berücksichtigung der acetonlöslichen Seifen ist aber dann zu empfehlen, wenn an Stelle von fettsaurem Kalk harzsaurer Kalk zur Hersttellung der konsistenten Fette verwendet ist, weil letzterer in Aceton etwas leichter löslich ist. Man berechnet dann die Menge der löslichen Seifen aus dem Aschengehalt unter Zugrundelegung des mittleren Moleculargewichtes 300 der zugehörigen Säuren.

Durch Anwendung des Acetonverfahrens lässt sich die bisher oft recht verwickelte Prüfung der Gesamtzusammensetzung konsistentèr Fette erheblich vereinfachen, da von vornherein scharfe Trennung der festen Bestandteile von den flüssigen (öligen) erfolgt. Die öligen in die Acetonlösung übergehenden Anteile können aus Mineralöl, Harzöl, Teeröl, fettem Oel und Glycerin bestehen. Letzteres scheidet sich in der Regel als dunkelbraune dickölige wasserlösliche Schicht unter den öligen Anteilen ab. Die Kennzeichnung der genannten Stoffe nebeneinander erfolgt nach bekannten Verfahren und macht keine Schwierigkeiten.

Die in Aceton unlöslichen, aber in Benzol-Alkohol löslichen Seifen können nötigenfalls nach Zersetzung mit Salzsäure noch daraufhin geprüft werden, ob eine fettsaure oder harzsaure Verbindung vorlag. Im salzsauren Auszug kann gleichzeitig die Seifenbasis (ob Kalk oder Tonerde usw.) ermittelt werden.

Die Untersuchung der in Aceton und Benzolalkohol unlöslichen Mineralstoffe erfolgt nach den bekannten Verfahren der anorganischen Chemie.

Nach Vornahme der aufgeführten Bestimmungen ergibt sich der Wassergehalt der konsistenten Fette aus der Differenz, kann aber auch direkt nach dem Xylolverfahren ermittelt werden.

VERGLEICHENDE BESTIMMUNG DES SEIFENGEHALTS HELLER KONSISTENTER FETTE

Seifengehalt
ermittelt durch

No.	Titration %		Gewichtsanalyse %	
1	13,2 13,5	13,4	14,0	
2	11,7		11,5	
3	9,8 9,9	9,9	11,0 11,2	11,1
4	13,4 13,8	13,6	14,3 14,3	14,8
5	8,9		8,3 8,6	8,5
6	13,2 13,5	13,4	14,5 14,6	14,6
7	15,0		15,3	
8	17,1		16,9 17,0	17,0
9	21,1		21,5 21,6	21,6
10	17,0		17,2	
11	23,2		23,6	
12	24,1		23,7 23,8	23,8

THE STRUGGLE BETWEEN WHITE PIGMENTS IN EUROPE

GASTON DE PIERRES
London, England

I have for many years past followed the struggle between the white pigments used in Europe and a few words on the subect will, I hope, be of some interest to many of those who in the new continent have not had an opportunity to follow as I have the various phases of the fight, and also the methods adopted by various European Governments against white lead.

In many quarters it is a struggle to death and aims at nothing less than the complete disappearance of an industry, which up to now has been the most important in the paint trade.

I do not intend to speak of the causes in which the struggle originated. Others more competent than I am (members of the Medical Profession) are better qualified to deal with that side of the subject. However, it is the duty of the paint technologist to follow with impartiality the evolution that is taking place; to appreciate and investigate all the properties and improvements of the substitutes; and especially to prepare himself to modify his industry in conformity with the new laws and circumstances.

In France the Government is taking most energetic measures to enforce the application of the law of 1909, which completely forbids the use and manufacture of white lead on the 1st of January, 1915.

Lately the Government became aware of the abuse that was made of certain denominations and rightly held the view that if spurious products and pigments of bad quality were sold to the painter the public would still consider that white lead could not be dispensed with. In consequence the Government, having ascertained that the description of white zinc that was used for all pigments, contained zinc salts and that in one case, for instance, the War Department had been supplied with a so-called white zinc, which when analyzed was found to be lithopone, containing 7% of Zns, it was decided to appoint a commission, composed of experts and technologists, to discuss and possibly find a way of suppressing these abuses. This Commission completed its work some few months ago and laid before the Government its finding, submitting also its propositions. These will shortly be printed and a regulation passed, in which zinc oxide will be defined according to law in conformity with up-to-date knowledge. The official text is as follows:

"Article 4.

"The description 'ZINC WHITE' (Blanc de Zinc) with or without qualification shall be applied exclusively to oxide of zinc used in painting and containing not more than 5 parts of impurities derived from the ore in 100 parts. Such impurities may consist of lead compounds provided they do not exceed 3% calculated as metallic lead (*Pb*)". I need not tell you that had a definition like the foregoing been proposed say fifteen years ago, it would have been unanimously protested against.

Many new facts of importance have resulted from this proposition.

Firstly: For white zinc the Commission completely abandoned the principal of chemically pure ZnO, and the ZnO containing lead salts up to the percentage mentioned in the description I have just given you is considered as the prototype of the product in constant use. It is not improbable that the French Commission was to a great extent inspired by the condition of affairs in Sweden. While England, France, Germany and some other countries were busy discussing at length the effect upon the technique of painting if the use of white lead were prohibited, and while the sworn partisans of white lead were expressing the most amusing opinions on the subject, there were still two countries in Europe where the use of white lead was extremely restricted compared with that of white zinc, and these countries were Sweden and Norway. There is not a single factory in Sweden for the manufacture of either white zinc, lithopone or white lead. The *official* statistics give the following figures for the years 1904–1910 (those for 1911 are not yet known):—

White Zinc and Lithopone		White Lead	
1904:	3,032,939 kgs.	1904:	511,253 kgs.
1905:	3,090,787 kgs.	1905:	512,832 kgs.
1906:	3,690,950 kgs.	1906:	558,946 kgs.
1907:	3,844,760 kgs.	1907:	557,820 kgs.
1908:	3,766,210 kgs.	1908:	509,759 kgs.
1909:	3,653,051 kgs.	1909:	509,548 kgs.
1910:	4,274,903 kgs.	1910:	501,314 kgs.

The above figures show that in 1910 consumption in Sweden of pigments based on zinc was 8½ greater than that of white lead. In Norway the consumption of zinc pigments is 20 times larger than the consumption of white lead.

It will, therefore, be apparent that white lead is steadily on the downward grade, while zinc and lithopone are constantly progressing. Moreover, as there is no duty on either white lead or zinc, it is clear that the statistics cannot be vitiated by such factors as economy, especially as no legal restriction limits the use of white lead. As the climate of Sweden is especially severe and marked by very great variation in temperature, this state of things constitutes an experiment in which the conditions are remarkably severe and in favour of white pigments based on zinc, and it must be regarded as much more far-reaching than theoretical considerations or local tests prescribed by Committees appointed to study the question.

Inquiries were made which revealed the fact that the bulk of the zinc white used in Sweden contained a slight percentage of lead, i. e. from 3 to 4% in the form of basic lead sulphate. Great was the stupefaction of certain specialists consequent upon this discovery, since it has been almost an article of faith that the highest quality in a white zinc was its absolute purity so to speak. All the specifications emanating from public bodies stipulated a maximum of from .5 to 1.0% of foreign matter. On the other hand, so long as the analysis of the product agreed with the specification, these public bodies were not at all anxious to ascertain whether the zinc supplied had, or had not, any pigmentary value. As a matter of fact, the physical condition of the product—a factor which plays such an importnat part in the value of a paint material—was absolutely lost sight of.

There is also very little doubt that the French deliberations must have been influenced by the example set by the Belgium State railway, on which white lead and red lead have been prohibited for the last five years. I have before me a recent publication from Mr. Souris, Chief of the Painting Department on that system, and few of the passages therein contained are interesting, since this gentleman up to a few years ago held a very strong brief in favor of white lead. This being taken into consideration, his pronouncement today cannot fail to be of the highest importance.

This is what he says:—"For the last 5 years the Belgian Railways—the most important of our Administrations—have made exclusive use of white zinc, which has everywhere superseded that of white lead. Moreover the white zinc in use is an oxide containing a slight proportion of basic sulphate of lead; the latter is neither precipitated nor mixed mechanically with the zinc oxide, but is obtained by sublimation of the ore in the furnace itself simultaneously with the zinc oxide. Each molecule of ZnO is, so to speak, impregnated with a very minute quantity of salts of lead; hence the very special physical state characteristic of this product."

The writer adds:—"The great advantages possessed solely by leaded zincs are economy, innocuousness, good paint-forming properties, covering and spreading power, etc.; all these qualities point to its suitability for both interior and exterior decoration of public buildings, such as Hospitals, Sanatoria, Amphitheatres, etc. I ask for no further proof than the example of the Belgian Railways, to which I would like to refer once more.

"This Administration uses white zinc *to the complete exclusion of White Lead* for all painting contracts *for both inside and outside work*, i. e., for building and working plant which are much exposed to the inclemency of the weather, besides all kinds of deleterious fumes.

"In spite of these extremely unfavourable conditions, the zinc paint coatings give the Authorities entire satisfaction.

"We may, therefore, conclude, and with still more reason, that White Zinc can advantageously and completely replace White

Lead for all ordinary painting, inasmuch as the conditions which prevail are generally much less severe."

It is noteworthy that only a few years ago this same writer declined even to consider the possibility of using other than absolutely pure white zinc; it is therefore interesting to note that he has entirely altered his opinion after 5 years' use of leaded zinc in the important departments of the Belgian Railways under his control.

In France the matter has been taken so seriously that today apparatus has been designed and constructed for ascertaining rapidly the percentage of Pb. in paints. This is done by means of dissolution of the paint and colorimetric analysis. I understand that these instruments will be placed in the hands of the inspectors.

The French Government, following the same procedure as they followed for Zinc Oxide, and desirous of avoiding any adulteration, made a point to legally defining lithopone in the following manner:—

"Article 6.

"The description 'Lithpone' (Lithopone) with or without qualification shall be applied exclusively to the product containing in each 100 parts of mineral matter, 99 parts at least of compound of zinc and barium sulphate. The latter shall be derived exclusively from the barium sulphide used in the process of manufacture. The products must not be sold unless the labels and invoices state the composition in terms of zinc sulphide."

In the past great difficulty was experienced in finding out whether barytes has been added to Lithopone. Today the problem has been solved and polarized light will be employed to determine the presence of natural barytes in the pigment.

In England the Government some time ago appointed a Commission which to a great extent has done over again the work of the French Commission, and I believe no one in Great Britain would be surprised to see it come to the same decision. One point has, however, caused a good deal of anxiety to the British authorities, and that is to know whether it would be possible to find sufficient zinc pigment to replace the 60,000 tons of white lead used annually in England, and that without disturbing the economic conditions. If one takes into consideration the increased favor with which lithopone is regarded in England it is possible to estimate approximately that 33,000 tons of ZnO calculated in the metallic state would be needed to produce 30,000 tons of ZnO and 30,000 lbs. of lithopone. Since the actual world production of spelter is 850,000 tons and that this production increases from 40,000 to 50,000 per annum, I think no one need have any anxiety that the raw material will be wanting, especially as it is possible to use for the manufacture of zinc oxide by the direct process low grade ores which cannot very easily be utilized for spelter making. Those who are qualified to express an opinion on the subject are of the opinion that even where this large quantity of zinc pigment needed no substantial increase in the price need be anticipated. On the contrary, it is thought that the reverse might be the case and that the increased production on large scale might cause a fall in prices as has been the case with lithopone within the last few years. Taking this into consideration it is most probable that the British authorities will not stop before these objections. There can be no doubt at the present moment the British Government finds itself with only two alternatives, restriction or suppression. All those who are inclined to compromise, and we know that this is essentially a British characteristic, would undoubtedly favor restriction, but unfortunately everywhere it has been found that restriction did not produce the results that were expected, since it is almost impossible to frame laws which can be enforced. Consequently such laws are dead letters. This was the case in France where these laws having been proved inefficient, it was found that suppression was the only remedy. Also in Belgium similar restriction laws were passed three years ago, but have never been observed. It has been found practically impossible to compel workmen to abide by these regulations, and today the Workmen's Syndicate and Trade Union are energetically supporting the suppression of white lead, and are posting all over the country posters in which they say:—

"Le travail doit faire vivre et non mourir."

A new projected law is now being put before Congress and I hear that it has every chance to be passed, since four years ago restrictions were adopted instead of complete suppression by a majority of one vote only.

Now, since I have approximately shown you the situation in Europe in some of the principle states, let us see what will be the possible consequences:—Undoubtedly the rapid increase in the sale of ready mixed paint somewhat on the same system as that practised in this country. Everywhere the paint user realizes the fact that paints ready-mixed for use are not only better but more economical than those prepared by the old and obsolete method where the preparation of protective or decorative coating was left to more or less inexperienced hands. Another consequence, of greater importance still from a scientific point of view, is the enormous amount of work being done by everyone connected with this industry to improve the manufacture and physical properties of all the zinc pigments.

It seems to be quite clear that many of the contrary conclusions arrived at by experts of good faith in the comparisons between white lead and zinc pigment is simply due to the want of appreciation of the importance of the physical state.

For instance, how many manufacturers confidently started making lithopone on account of the apparently simplicity of the process. All, of course, succeeded in making a chemical product containing 71% BaSou and 29% ZnS, but a great number of them were compelled to give up manufacturing since they were not able to produce a lithopone with any pigmentary value. A great many valuable improvements have been made of late in the manufacture of this important pigment.

Two of the greatest defects of lithopone, as you know, have been darkening (due to photogenic properties) and chalking.

The permanency of lithopone has engaged the attention of many chemists and it is now possible to make lithopone quite permanent when used as an oil paint. To obtain perfect fastness to light you must have a lithopone absolutely free from chloride. This, of course, sounds quite simple, but in practise is most difficult to obtain, especially when a manufacturer uses the chloride roasting process to extract zinc from poor ores, as is the case in some important European factories.

I will not leave the question of permanency without mentioning the want of logic of certain manufacturers in testing lithopone for fastness to light. With many of them it is customary to put the lithopone in a glass tube filled with water. If the lithopone darkens they wrongly come to the conclusion that it will behave similarly when used in oil paint. The conditions not being similar, the test is of no value, since I have known lithopone which did not darken in water and changed very quickly in an oil paint, and I have found that this was due to the presence of silicate of soda in this lithopone; but, on the contrary, I often found lithopone changing in the water test and yet remaining perfectly permanent when exposed to the air and light of an oil paint. Consequently, this pigment should always be tested in the way in which it is to be used.

With regard to chalking, this is of great importance, but is quite easy to explain. It is due to the poor oil assimulation on account of extreme calcination. This tends to make the product less amorphous and requires less oil in the grinding. No doubt it is more economical for the grinder, but lithopone which has little affinity for oil does not stand well and chalks very quickly and it will not resist washing.

Manufacturers in Europe, and especially in England, where good quality is much appreciated, insist upon the use of a lithopone requiring 15% to 16% of oil in the grinding.

Let us now examine the progress made in the manufacture of zinc oxide. One of the most interesting features is an improvement on the Wetherill process. A manufacturer in Europe working on this process, starting from raw material containing lead, has succeeded on obtaining a very white and pure oxide absolutely free from lead and as white as the red seal brand obtained by the French process. The principal advantage of this French product is not so much its purity as its fineness and extraordinary softness which makes it a valuable pigment for enamel manufacture. The separation of the zinc salt from the lead salt constitutes a most remarkable scientific achievement.

The struggle between white lead and the other pigments has brought forth numerous improvements in our industry and I have brought them forward in the hope that they might be of interest to those who are far away from the field of battle.

A METHOD FOR THE DETECTION OF ADULTERATION OF CHINA WOOD OILS

Louis Samter Potsdamer
Philadelphia, Pa.

About July 15th of this year there appeared a paper published by the New York Produce Exchange, which spoke of the Bacon Method for the detection of at least 5% Adulteration of China Wood Oils. The paper sets forth that the suspected oils were to be placed in a bath of between 280° and 285°C for 8½ or 9 minutes. To detect adulteration after polymerization the oils were to be cut with a knife, the pure offering little or no resistance to cutting and showing a clean cut surface; while the adulterated under similar treatment displayed a ragged cut, or else it could not be cut at all.

This was given a fair trial in the Research Laboratory of Toch Bros. Paint Factory, with little success, until I decided to note the temperature of polymerization of the various samples, adulterated and pure. I had several samples of the pure oil, and these I made up into stock solutions as follows:—

Pure,
5% Adulteration with Soya Bean Oil,
10% " " " " "
5% " " Paraffine Oil,
10% " " " "

(Soya Bean and Paraffine Oils were chosen as representative of vegetable and mineral oils, respectively.)

The apparatus used was such that a bath of oil, (Pure Soya Bean Oil), was placed in a nickel pot of about 8 inches diameter. In this were suspended 2 test tubes, arranged to act as an air bath. The samples were placed in tubes of slightly smaller bore and in turn in the air bath. Thermometers were suspended in these tubes so that the mercury bulbs extended below the middle of the oil under examination.

The bath was first heated to a temperature between 510° and 525° F and the sample tubes, filled so that the oil surface did not extend above the surface of the bath, then placed in position. They were allowed to remain in this position until polymerization just set in, stirring once in a while with the thermometers.

At the point of polymerization the temperature was noted and the tubes withdrawn from the bath. Referring to the tables one can see that adulterations as low as 5% cause a very perceptible drop in the temperature of polymerization.

I made only three sets of oils but from these I obtained results on which I base my method for the detection of adulteration. I found that the first 2 oils under examination had an average polymerization temperature of 553° and the 3rd. (a mixture of 2 supposedly pure oils, received at Toch Bros. Factory for testing), at a somewhat lower temperature.

Disregarding such a small discrepancy, 15° F., we notice that the adulterations caused a decided drop in the polymerization temperature, and as Soya Bean Oil is handiest to the oriental, we may expect adulteration with this.

By the method herein described, an adulteration of 5% could be detected. To settle this finally I offer this suggestion; that the American Society for Testing Materials now working on the standardization of Soya Bean and China Wood Oils, add the above to their tests and so obtain a standard temperature of polymerization in the manner described, and all oils meeting such a temperature (or those within small range) call pure. It would then be a very simple matter to detect adulteration.

Supplementing the polymerization test were determined the Specific Gravities of the Oils under standard conditions (60° F.) It was noticed that the higher the percentage of adulteration the lower the sp. gr., and further when the adulteration was mineral oil, the sp. gr., was lowered at least 4 times as much as with a similar percentage vegetable oil.

Polymerization Temperatures

Sample	Set 1	Aver.	Set 2	Aver.	Set 3	Aver.
Pure	551 554	553	552 554	553	538 535	537
5% Soya	522 516	519	520 514	517	505 500	503
10% Soya	502 498	500	476 474	475	498 500	499
5% Paraffine	516 513	516	518 516	517	494 500	497
10% Paraffine	513 515	514	489 492	491	488 492	490

Sample	Sp. Gr. at 60° F.		
	Set 1	Set 2	Set 3
Pure	0.9423	0.9416	0.9409
5% Soya	0.9417	0.9407	0.9391
10% Soya	0.9410	0.9401	0.9381
5% Paraffine	0.9348	0.9350	0.9326
10% Paraffine	0.9330	0.9323	0.9310

Iodine values were also made in the samples, with the following results:

Samples	Set 1	Set 2	Set 3
Pure	160.4	158.8	150.5
5% Soya	158.0	155.4	147.8
10% Soya	156.2	151.9	141.6
5% Paraffine	155.2	150.8	140.5
10% Paraffine	143.9	143.4	136.8

The impurities make quite an appreciable lowering in the Iodine Values.

THE COATING POWER AND THE HIDING POWER OF PAINTS

GUSTAVE W. THOMPSON

As the title of this paper would indicate, we distinguish between two qualities which paint possesses: one to produce a coat upon the surface painted and the other to hide the surface painted. Often the expression "covering power" is used to include one or both of these expressions. Usually "covering power" refers to the power to hide the surface; but it has also been used as referring to the power the paint possesses to coat a surface. We would distinguish between these two qualities. We believe that as this paper is read, the desirability of such distinction will appear.

A little thought will clearly bring out that there is no necessary connection between the power possessed by a paint to coat a surface and its power to hide a surface. We speak here of power in a quantitative and relative sense. We refer to a power which can be measured and which varies with the composition of the paint and the way it is applied. A paint having a coating power twice that of another would, in the sense we use the word "power", give a coating twice as thick; and a paint having a hiding power twice that of another, would give a coat that would hide twice as well.

The purpose for which a properly designed paint is used will affect the relative importance of coating power and hiding power. A paint closely approaching a varnish, that is, having very little pigment in it, may be designed so as to produce a thick coat having very little hiding power; and on the other hand, a paint like a great many of the flat wall finishes on the market may have a reasonably high hiding power but produce a very thin coat, and so could be said to have a low coating power.

Directing our attention first to the coating power of a paint, we find that this power is a function of the spreading rate, the percentage by volume of non-volatile materials it contains, and the gain or loss in the drying of these non-volatile materials. Other factors may also exist such as the porosity or roughness of the surface painted, but it would seem desirable that in our discussion we limit ourselves to the three factors given above, recognizing, of course, that this limitation is an artificial one adopted for the purpose of giving us a practical conception of the subject before us.

The spreading rate at which paint is applied is dependent upon so many apparently variable factors that at first thought it would seem that any rational inquiry into the spreading rate at which a paint is to be applied would be futile. We, of course, can see at once that the greater the spreading rate, the lower the coating power, and consequently the spreading rate becomes a factor in the denominator of any mathematical expression we may construct representing the coating power of a paint. Furthermore, the spreading rate is affected by the consistency of the paint; the thinner the paint is, the greater its spreading rate, etc. Here we are confronted with another difficulty which will have to be cleared up.

We must make another assumption to start with, and that is in comparing paints, the comparison is to be made on comparatively smooth surfaces, say—either the hard prepared and filled surface of wood or the surface of polished iron. We can assume also if we desire that all paints have the same standard spreading rate, but this assumption would hardly be feasible, as paints are known to vary very considerably in their spreading rate. Paints when applied over smooth surfaces vary in spreading rate from 300 to 1800 square feet to the gallon; and it would seem best that in studying the coating power of a paint, we actually make a spreading rate test, using either of the surfaces referred to, and in our opinion preferably polished sheet iron. The figure in any case obtained is a relative figure and would probably vary with all paints in the same direction. To determine the spreading rate the best method which we have found is to make a number of tests, spreading the paint in one case at 300 square feet to the gallon, and in other cases at 600, 900 ft., etc., until the maximum rate is obtained; that is, until it is found impracticable to spread the paint beyond a found spreading rate. The limit to which paint can be spread is fixed by obtaining a continuous and smooth coat.

Our second factor referred to above is the percentage of non-volatile materials present in the paint. It is evident in comparing paints that if they have the same spreading rate, the coating power of the paint is proportional to the percentage of non-volatile constituents present.

The change in volume which takes place due to the oxidation of the non-volatile vehicle has been studied very considerably by A. H. Sabin, and it would appear that to start with, there is a probable increase in volume, but that later on there may be a actual contraction in volume, due to the giving off of oxidation products from the vehicle. If this factor in the coating power of a paint were necessarily to be considered, our study of this subject would immediately stop for the reason that what takes place in paints according to the various conditions of exposure which result in the non-volatile vehicle increasing or decreasing in volume, is so intricate that one could not reason at all on the subject nor reach any satisfactory conclusion. We believe, however, that it would be fair to assume that the change in volume of paints during the drying is fairly uniform; that is, that the increase or decrease in volume may be considered as a constant. If we make this assumption (and we appreciate that it is an assumption) we get to a point where we can obtain a coefficient for the coating power of paint. If we represent this coefficient by C.P., the percentage of non-volatile matter as N. V. and the spreading rate as S. R., we get the following equation:

$$\text{C. P.} = \frac{\text{N. V.}}{\text{S. R.}}$$

C. P. in any case will represent the relative coating power which a paint possesses.

We believe that the coating power of a paint is a very important factor in estimating its value. Where there is no volatile matter present as in the case of many paints for protective purposes, then the coating power depends entirely upon the spreading rate; but in the case of paints intended for inside use, as we have already pointed out, which contain a high percentage of volatile matter, there the coating power is dependent also on the percentage of non-volatile materials present. Furthermore, the use to which a paint is to be put must be considered. If it is intended to be washed or if it is to be subjected to much abrasion, it should have a reasonably high coating power.

Coming now to the second part of our subject, the hiding power of paint, we find presented to us a still wider field for investigation than the coating power presented. The field is so large that while we will endeavor to treat many phases of the subject, there will still remain very many which we cannot touch. The hiding power depends upon optical phenomena. Furthermore, it is a physiological property. The perception of hiding power is dependent upon the eye, but although we might be justified in developing our subject to include those rays which are invisible to the eye, it is not our intention to do so.

Considering the subject first with reference to the eye, we have, in the first place, the sensitiveness of the eye to differences in color and illumination.

2nd: We have the differences in color and reflecting power which may exist between paints.

3rd. We have the color and luminosity of the surface painted.

On the question of luminosity, Fechner's law throws a little light. It is stated as follows:

". . the differences in sensations vary as the logarithm of the ratio of the stimuli producing the differing sensations."

Fechner's law is based on the observation that the eye can, as a rule, note differences in illumination only when these differences are greater by a certain amount, no matter what the illuminations may be, and usually this difference is about 1%; that is, the eye can note differences of 1% and over in the intensity of illumination, no matter what that intensity may be. From this we will note that the luminosity of a surface painted and the luminosity of the paint applied affects the optical perception of hiding power. If a surface has a luminosity of 99, and the paint applied has a luminosity of 100, the eye would not notice the difference in luminosity between the surface painted and the paint applied, and consequently the paint applied need not have a high hiding power. If, on the other hand, the surface painted has a luminosity of 1, and the paint applied a luminosity of 100, it will readily be seen that the paint should have a high hiding power.

As the eye varies in sensibility to different colors, so this same power of perceiving differences between surfaces painted and the paint surface, is affected by the colors of the surface and the paint applied. It would appear that the eye will note smaller differences between colors that are in contrast with each other than it will where the colors are similar.

With this preliminary statement, we will take up the question of the hiding power of paint more in detail. In general, this hiding power depends upon the capacity of the paint. By opacity we mean the power to absorb transmitted light. This power is best expressed as a decimal fraction of unity and is independent of the intensity of the light; that is to say, an object having a certain opacity, say—.50, will absorb 50% of the light it receives and transmit 50% independent of the intensity of the light received. Of course, we refer only to the light which enters the object and we have nothing to do with that which is reflected by it, although it is probable that the reflecting power of paint will have to be considered in any final reasoning on the subject.

If we apply these principles, and take for illustration sheets of paper each having the same opacity of .50 and hold one up to the light, 50% of the light received will pass through it. If we place two superimposed up to the light, the second will transmit 50% of the light it receives and the two together will transmit only 25% of the light received. If we look through three superimposed sheets, 87½% of the light will be absorbed, and only 12½ % will be transmitted. The absorption of light by these successive superimposed layers may be represented by a logarithmic curve. We show here several such curves of assumed opacity. (See print attached hereto.)

If we apply this to the subject before us, the hiding power of paints, and assume instead of layers, units of thickness, we find that the opacity varies in the same logarithmic curve, the character of which is affected by the opacity of the paint.

We give here the development of a formula for the light that passes through any number of units of thickness of paint:

L = the light passing through any number of thickness units.
S = the light absorbed by any thickness unit or units.
a = the light striking the first surface.
A = the ratio $\frac{L}{a}$
n = the number of units of thickness.
P = the constant opacity of each unit of thickness in the form of a decimal fraction of unity.

Light passing through no unit of thickness:

$$L_0 = a \qquad = a$$

Light passing through one unit of thickness:

$$L_1 = a - Pa \qquad = a(1-P)$$

Light passing through two units of thickness:

$$L_2 = (a-Pa) - (a-Pa)P \qquad = a(1-P)^2$$

Light passing through three units of thickness:

$$L_3 = \{(a-Pa) - (a-Pa)P\} - \{(a-Pa-(a-Pa)P\}P = a(1-P)^3$$

$$L_n = \qquad a(1-P)^n$$

$$\frac{Ln}{a} = A_n \therefore$$

$$A_n = (1-P)^n \qquad \text{General formula}$$

To use this formula we should, of course, have a means of determining opacity in standard terms. In this paper we cannot do much more than present the problem with certain suggestions as to methods of determining opacity. For paints we would suggest that opacity be expressed in the decimal fraction of unity using a paint thickness of .1 mm. The opacity which a paint .1 mm. in thickness possesses we will refer to as the "coefficient of opacity." Where the word "opacity" alone is used, it will refer to the aggregate opacity of the paint.

The practical application of opacity testing may be seen in the following example:

We have referred to the observations on which Fechner's law is based, namely: that the eye can perceive differences in luminosity of about 1%. It would appear, therefore, that the difference in luminosity of a surface painted and the surface of a paint should be less than 1%. Now, if we have a paint having an actual opacity of .90, it will absorb 90% of the light received by it and the surface painted will receive 10%. Assuming that all of this 10% is reflected to the eye, then the paint will absorb 90% of that, and leave only 1% to come to the eye. Under these conditions the paint can be said to have sufficient opacity and the surface to be well covered.

We have been endeavoring for some time past to construct an apparatus for measuring the opacity of paints. We are unable at this writing to report any results obtained with this apparatus. Later on we may have something of value to report. The ideal apparatus would be one that would start with a standard test piece of opacity obtained by photometric methods, and then by comparing various paints with this standard test piece, determine the thickness of paint necessary to produce opacity equal with the standard and then, from the formula given above, calculate to the coefficient of opacity of the paint. Such an apparatus should be constructed so that light of varying intensity could be used, and also light varying in color which could be obtained by passing it through color filters.

With such an apparatus constructed, it could be determined whether a paint on drying increases or decreases in opacity; also whether paints containing volatile matter increase or decrease in opacity on the evaporation of the volatile matter. The tests should be run preferably on wet paint; but it may be necessary to correct the readings obtained to what would be obtained when the paint dries.

If we obtain the coefficient of opacity by the above formula, we can determine what the opacity is for any thickness of paint; and having also determined the spreading rate of the paint as outlined in the first part of this paper, the hiding power of the paint can be measured.

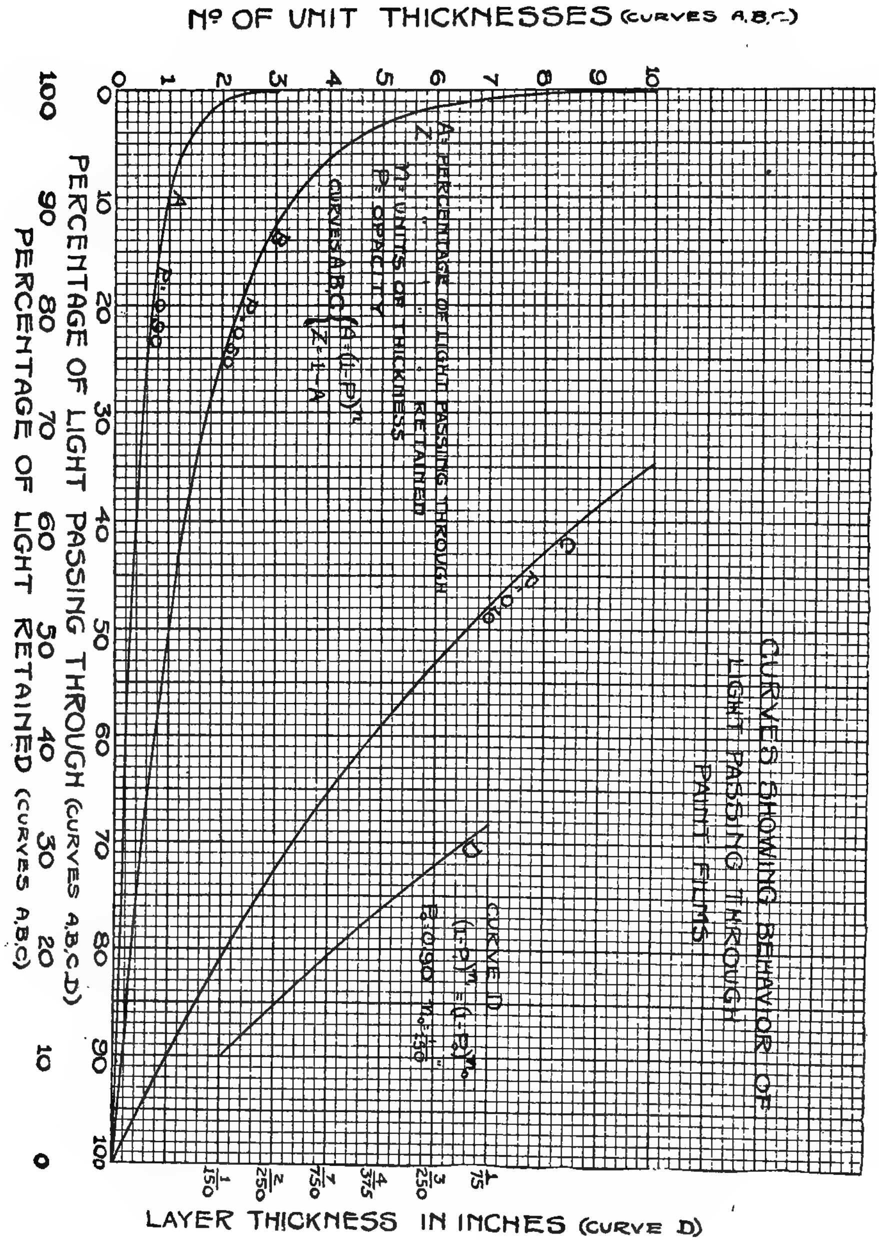
Pigments and mixtures of pigments can also be tested for opacity. It may be improper, however, to refer to dry pigments having opacity. It certainly would be improper to measure the opacity of pigments with air as a medium. For the purpose of obtaining the opacity of pigments, it would appear that it would be best to use a standard non-volatile vehicle such as linseed oil. We know that the percentage by volume of the pigment present affects the opacity of a mixture of a pigment with linseed oil. What the nature is of the opacity curve of a given pigment mixed in various proportions with linseed oil, we do not know. We do know that it is an ascending curve, but whether nearly a straight line or not remains to be determined. With the apparatus referred to we hope to obtain information on this point. We believe that all comparisons of pigments for opacity should be made upon the volume basis, preferably on the formula of 75% by volume of linseed oil and 25% by volume of pigment. This would operate satisfactorily with white lead. Where a different formula is necessary, it should still be by volume compared with a similar volume of some standard pigment. With colored pigments, the color screens referred to could be used. It would be very interesting to investigate the effect of the various physical properties of pigments upon their opacity. We know, in general, that the finer the pigment the greater the opacity. Perhaps it would be possible for us with such an apparatus to obtain a coefficient of fineness based upon the differences in opacity. We know, in general, also that the higher the refractive index of a pigment is over that of the vehicle, the greater its opacity. Perhaps it would be possible for us also to determine the refractive indices of pigments in the same apparatus. Perhaps we could also discover other factors in opacity.

There has been a great deal of discussion especially in a German periodical (Farben-Zeitung) recently on the relation between strength or tinting power and opacity, some claiming that there is a direct relation and others that there is an inverse relation. Most of these discussions are academic and not based on practical tests. There are reasons for believing that the relation between strength and opacity is a direct relation. These reasons are as follows: Strength increases as opacity does with the fineness of the pigment. In the case of white lead, for instance, its strength and opacity are both increased by grinding it finer.

2nd: Strength and opacity vary in the same direction with the change in the refractive index of the medium in which the pigment is ground. Thus, a lowering of the refractive index of the medium increases both strength and opacity for most pigments. This is observed in the whiteness of kalsomine when the medium—water, present is replaced by evaporation by the medium air. Both the strength and the hiding power or opacity of the whiting increases. There are other reasons for the belief that strength varies with opacity, but we do not accept this as demonstrated, and would only point to a means for such demonstration.

The usual method for determining strength is to rub up in oil a standard sample with a coloring medium in weighed proportions; and then rub up the sample to be tested with the same coloring medium, using more or less of it as may be necessary to produce the standard color, the strength being measured by the amount of coloring medium used. This method gives fairly satisfactory results, but takes considerable time and labor. Experiments which we have made with a disc machine indicate that the differences in color which are produced by mixing the coloring medium in varying proportions with a definite quantity of another coloring material is directly proportional to the quantity of the coloring medium used. For instance, we have found that in mixing white lead and lampblack, the results are distinctly impressionistic. The black becomes blended to the eye just as occurs on the rotation of the disc machine, and in the same proportion. Whether this is true of all coloring media we have not as yet been able to determine but the matter is under investigation.

We hope with the opacity measuring apparatus referred to and the disc machine to determine the relation between strength and hiding power and opacity. These pieces of apparatus are on exhibition at the reading of this paper.


CURVES SHOWING BEHAVIOR OF LIGHT PASSING THROUGH PAINT FILMS
Nº OF UNIT THICKNESSES (CURVES A,B,C)
0 1 2 3 4 5 6 7 8 9 10
PERCENTAGE OF LIGHT PASSING THROUGH (CURVES A,B,C,D)
0 10 20 30 40 50 60 70 80 90 100
PERCENTAGE OF LIGHT RETAINED (CURVES A,B,C)
100 90 80 70 60 50 40 30 20 10 0
LAYER THICKNESS IN INCHES (CURVE D)
$\frac{1}{150}$ $\frac{2}{250}$ $\frac{7}{750}$ $\frac{4}{375}$ $\frac{3}{250}$ $\frac{1}{75}$
A
P=0.90
B
P=0.50
C
P=0.10
D
A= PERCENTAGE OF LIGHT PASSING THROUGH
Z= " " " RETAINED
n= UNITS OF THICKNESS
P= OPACITY
CURVES A,B,C $\begin{cases} A=(1-P)^n \\ Z=1-A \end{cases}$
CURVE D
$(1-P)^m = (1-P_o)^{m_o}$
$P_o=0.90$ $m_o=\frac{1}{150}$"

GENERAL INDEX
REPORT OF EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

ORIGINAL COMMUNICATIONS

Volume	Section	
1	I.	Analytical Chemistry.
2	II	Inorganic Chemistry.
3	IIIa	Metallurgy and Mining.
4	IIIb	Explosives.
5	IIIc	Silicate Industries.
6	IV	Organic Chemistry.
7	IVa	Coal Tar Colors and Dyestuffs.
8	Va	Industry and Chemistry of Sugar.
9	Vb	India Rubber and other Plastics.
10	Vc	Fuels and Asphalt.
11	Vd	Fats, Fatty Oils and Soaps.
12	Ve	Paints, Drying Oils and Varnishes.
13	VIa	Starch, Cellulose and Paper.
14	VIb	Fermentation.
15	VII	Agricultural Chemistry.
16	VIIIa	Hygiene.
17	VIIIb	Pharmaceutical Chemistry.
18	VIIIc	Bromatology.
19	VIIId	Biochemistry including Pharmacology.
20	IX	Photochemistry.
21	Xa	Electrochemistry.
22	Xb	Physical Chemistry.
23	XIa	Law and Legislation Affecting Chemical Industry.
24	XIb	Political Economy and Conservation of Natural Resources.
25	Appendix, Original Communications, Sections I to Ve.	
26	Appendix, Original Communications, Sections VIa to XIb.	

27	Discussions.
28	Transactions and Organization.
29	Typographical and Authors' Changes; Index.